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

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

The following specification describes the nature of this invention.

PRICE: TWO RUPEES

This is an invention by KUPPUSWAMY VENUGOPALAN, Scientist, VEERARAGHAVAN ARAVAMUTHAN, Scientist and HANDADY VENKATAKRISHNA UDUPA, Director, MOHAMMED KAMALUDEEN, Senior Scientific Assistant and NEDUMARAM GOPALAN RANGANATHAN, Junior Scientific Assistant, all of the Central Electrochemical Research Institute, Karaikudi-623006, Tamil Nadu, India.

This invention relates to improvements in or relating to the production of electrolytic manganese metal.

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 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 60 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/cm^2 for the production of manganese metal which settles at the bottom.

EXAMPLE 1

Electrolyte:	Calcium fluoride and manganese fluoride in the ratio 1:1
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 ontained:	Manganese : 99.3 % Silicon : rest
Cell voltage and amp:	5.2V; 200 amp.
Current efficiency:	25%

EXAMPLE 2

Electrolyte:	Calcium fluoride and manganese fluoride in the ratio 2:1
Feedmaterial:	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 : 80% Iron : 17%
Cell voltage and amps:	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/cm^2 as opposed to 0.06 A/cm^2 in aqueous electrolysis.

Dated this 26th day of Dec. 1978.

Sd/-

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150471

THE PATENTS ACT, 1970

COMPLETE SPECIFICATION

(Section—10)

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

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi 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 :—

150471

This is an invention by KUPPUSWAMY VENUGOPALAN, Scientist, VEERARAGHAVA ARAVAMUTHAN, Scientist, HANDADY VENKATAKRISHNA UDUPA, Director, MOHAMED KAMALUDEEN, Senior Scientific Assistant, NEDUMARAM GOPALAN RENGANATHAN, 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/cm^2 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 fluorspar 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/cm^2 will result in the production of massive manganese which settles at the bottom. Thus, a high cathodic current density of 2-2.5 A/cm^2 can be maintained in fused salt electrolysis as compared to 0.04 A/cm^2 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 inter-electrode 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 fluorspar and manganese flouride at any ratio between 1 fluorspar to 1 manganese fluoride to 1 manganese fluoride to 3 fluorspar.

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.

Furthermore, by this process, it is possible to operate the cell at higher current densities, say, the order of 2 to 2.5 A/cm^2 as opposed to 0.04 A/cm^2 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 ores 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, electrolysing 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 alumino-thermic 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 3.8 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

Electrolyte :	Calcium fluoride and manganese flouride in the ratio 1:1
Feed material :	0.75 kg of pure manganese dioxide obtained by the decomposition of pure manganese carbonate
Temperature of electrolysis :	1200-1250°C
Quantity of metal obtained :	250 grams
Composition of the metal obtained :	Manganese : 99.3% Silicon : Rest
Cell voltage and amp :	5.2V ; 200 amp
Current efficiency :	25%

EXAMPLE 2

Electrolyte :	Calcium fluoride and manganese fleuride in the ratio 2:1
Feed material :	2 kg of -100 mesh manganese ore containing 40% manganese content as such (i.e. untreated ore)
Temperature of electrolysis :	1200°-1300°C

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 ration 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 : [illegible] Iron : 11.700% 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^{o}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 pyrelusite(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^{o}C with cathodic and anodic current densities of 2-2.5 and 9-10 A/cm^{2} 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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COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

COUNCIL OF SCIENTIFIC INDUSTRIAL RESEARCH.

COMPLETE.

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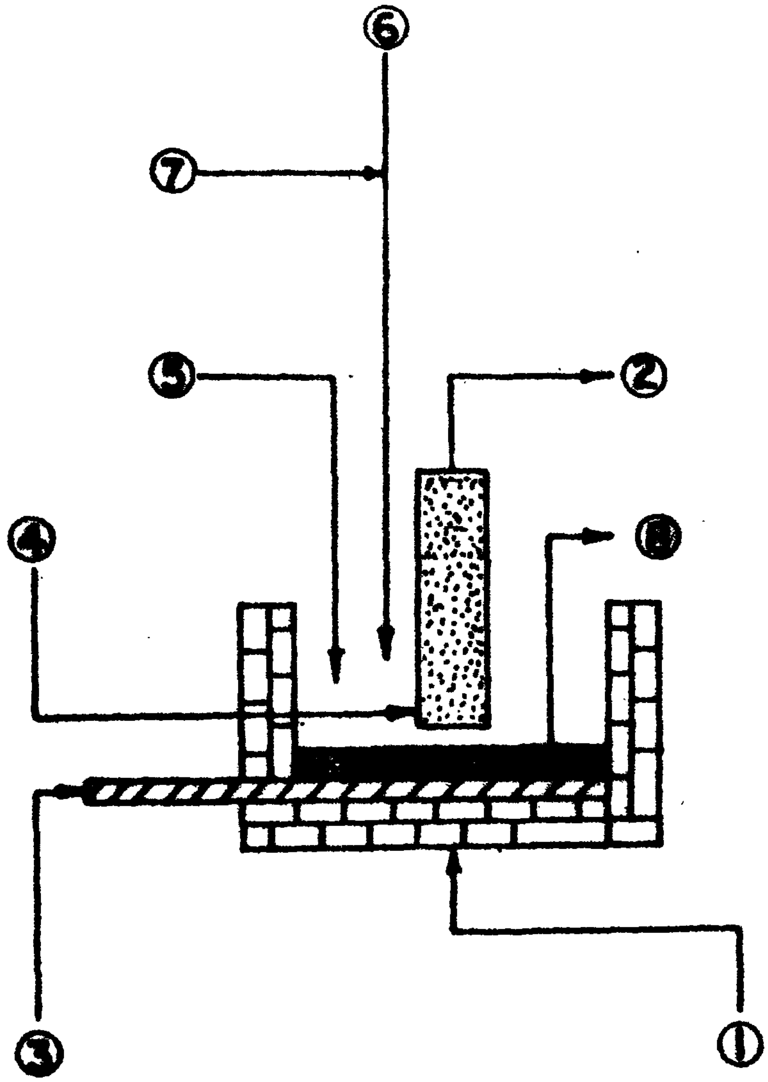

FIG. 1

m.s. [signature]

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