

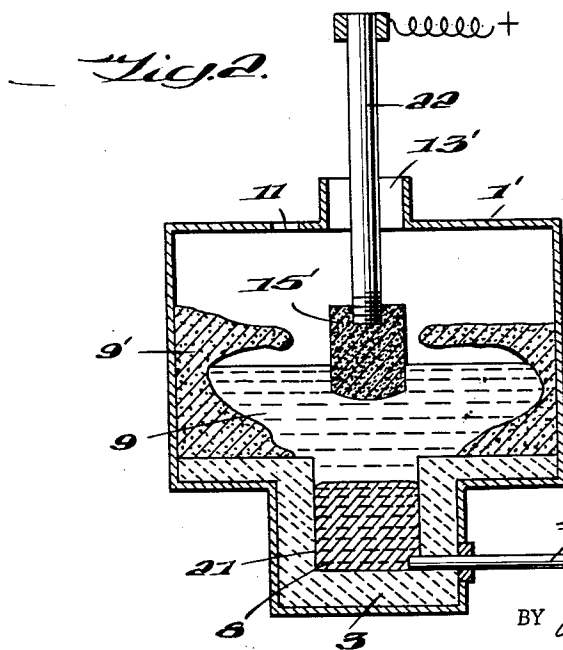
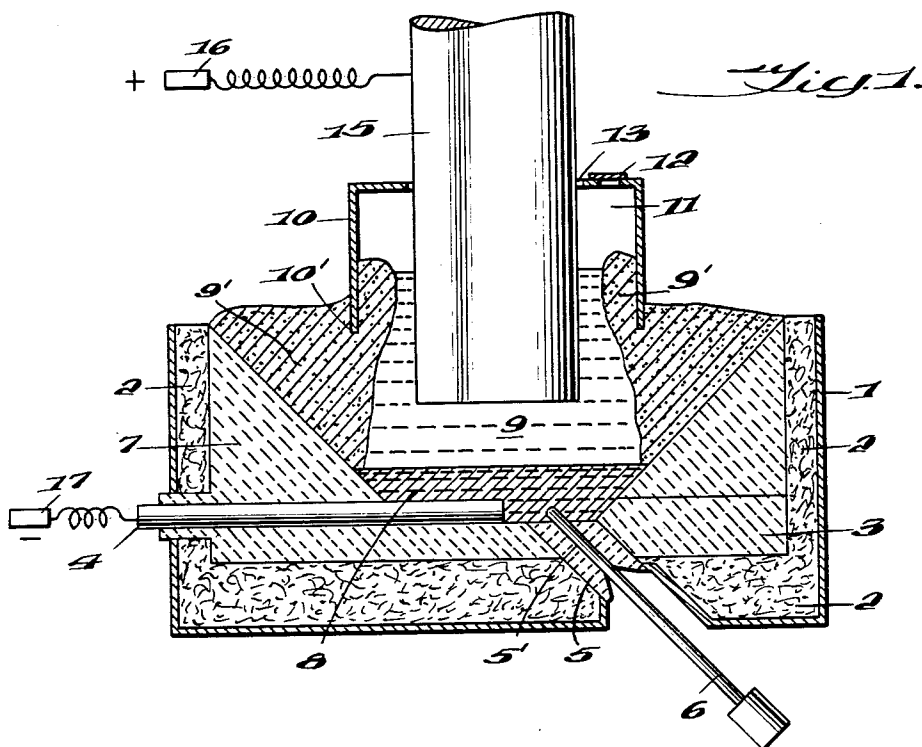
Jan. 23, 1962

J. Y. WELSH ETAL
PRODUCING MANGANESE BY FUSED SALT
ELECTROLYSIS, AND APPARATUS
THEREFOR

3,018,233

Filed Feb. 9, 1960

3 Sheets-Sheet 1



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Fig. 3.

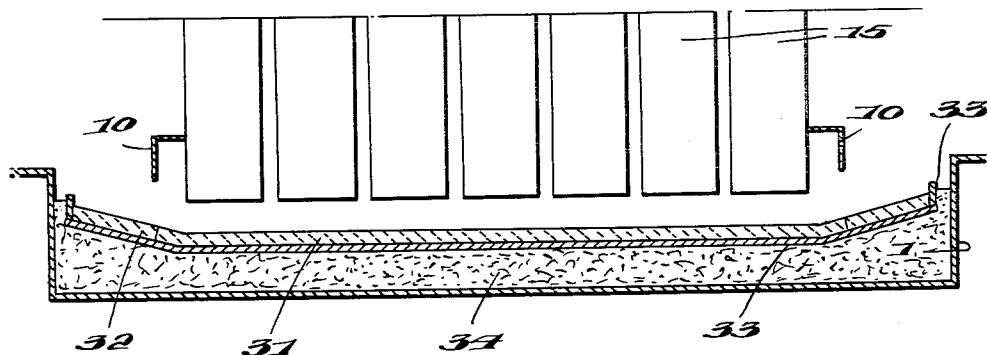
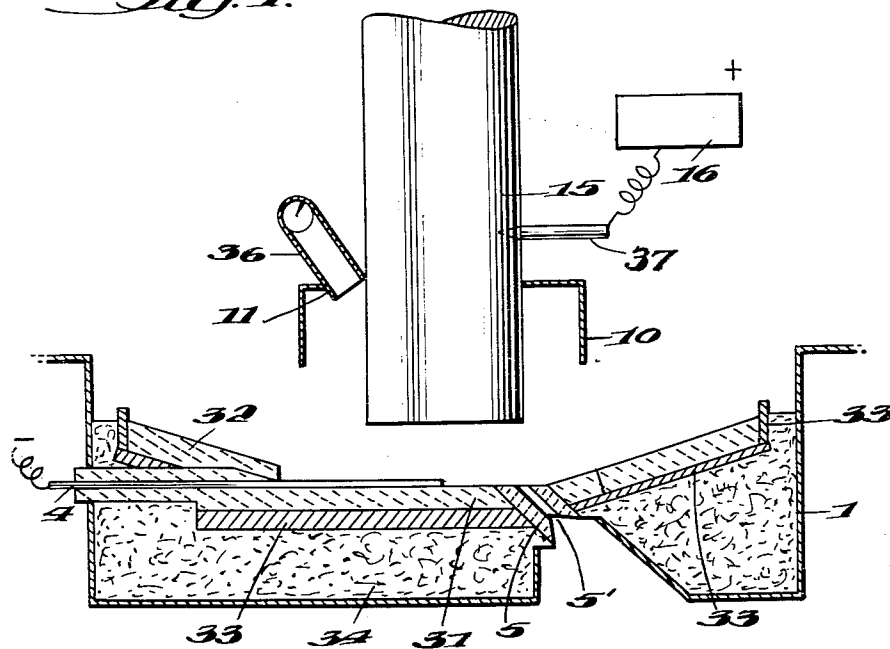


Fig. 4.



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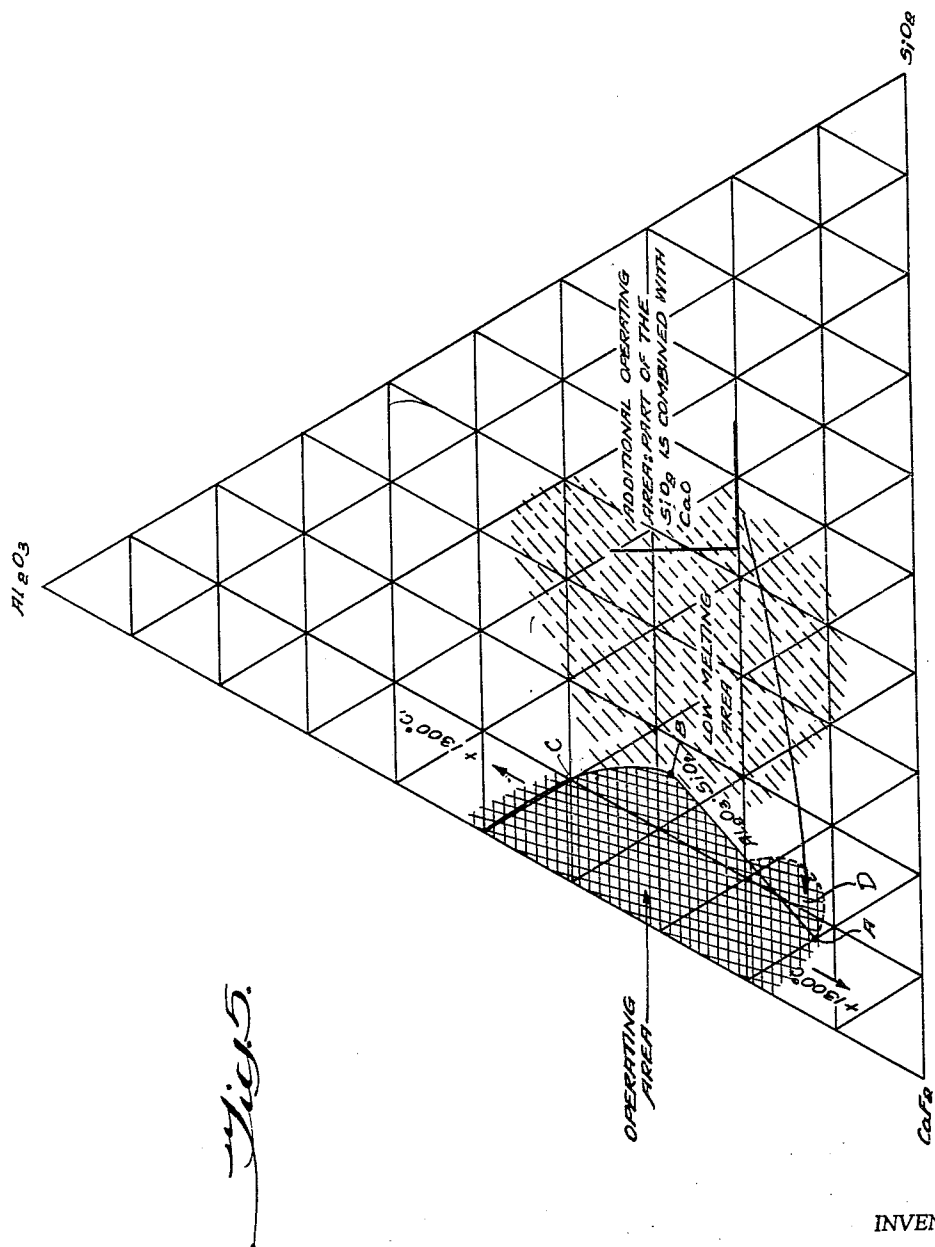
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3,018,233

PRODUCING MANGANESE BY FUSED SALT ELECTROLYSIS, AND APPARATUS THEREFOR

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This invention relates to the production of metallic manganese by electrolysis from fused salt systems, and is concerned with an improved process of, and apparatus for producing manganese, and alloys of manganese, very low in carbon by fused salt electrolysis.

It heretofore has been proposed—U.S. Patent No. 704,393, Simon—to produce manganese metal by electrolysis of a fused bath comprising calcium fluoride and a lower oxide of manganese. The metal product inherently was rich in carbon (7-8%)—due to the use of a carbon cathode and to the use of a feed containing free carbon—and hence had nothing to commend it over the conventional pyrometallurgical carbon reduction process.

More recently, it was proposed—in U.S. Patent No. 2,398,589, Mitchell—to lower the carbon content of the product metal by using a non-carbonaceous cathode and by lining with non-carbonaceous material that part of the cell which in the carrying out of the process normally would contact the product metal. However, the process entailed maintaining the fused bath (which consisted mainly of cryolite and sodium fluoride containing dissolved magnesia or alumina) at a temperature below the melting point of manganese whereby the product formed as an ingot of solidified bath stock containing reduced manganese, from which ingot the reduced metal subsequently had to be separated by melting in a separate vessel. The ingot, as produced in the electrolytic cell, contained from 25% to as much as 50% by weight of solidified electrolyte. When concentrated and purified, the final metallic product contained about 0.8% of carbon along with substantial concentrations of aluminum, silicon and other alloying impurities, and hence did not meet the need for low-carbon manganese of high purity.

According to the present invention, low-carbon manganese is produced, from a lower oxide of manganese, by a process which comprises establishing a fused electrolytic bath whose composition—consisting essentially of a mixture of oxides with at least 50% by weight of calcium fluoride—is stable against decomposition and volatilization at any temperature up to at least 1500° C. and which is molten and without solid phases at the desired operating temperature; confining this electrolytic bath within a solid skull of its own composition and above and contiguous to a pool of molten manganese; adding lower oxide of manganese (i.e., MnO, reduced MnO₂ ore, or MnO slags, consisting largely of MnO) to the bath while an electric current is passed through the latter from a carbon anode—partially immersed in the electrolytic bath—to the surface of said pool of molten manganese as cathode; maintaining the electrolytic bath at a temperature above the melting point of manganese and at such a temperature as to maintain molten at least the upper surface of the underlying pool of manganese; and intermittently tapping molten manganese from said pool.

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The expression “to maintain molten at least the upper surface of the underlying pool of manganese” is intended to mean that the pool of Mn should largely be molten, but that a frozen metal skull at the periphery of the metal pool is tolerable. As the process is carried out commercially, practically the whole pool—including of course the upper surface—is maintained molten and sufficiently superheated that the product metal is freely fluid and readily may be tapped.

In the carrying out of this process, the pool of molten manganese is supported on and contacted by a solid layer composed essentially of one or more refractory oxides which is or are non-reactive with molten manganese. Cathodic electrical contact with the molten metal pool is established and maintained by the provision of a conductive metal bar embedded in the refractory oxide layer and extending through the wall of the cell. As will readily be appreciated, the composition of this cathode contact bar should be compatible with the molten metal which it contacts, in order that any melting of the upper part of the bar will not result in undesirable alloying with the molten manganese. Since iron is not (usually) an objectionable alloying element in manganese metal, the cathode contact bar may be formed of iron or mild steel.

It is an important feature of the process (and apparatus) of the present invention that the heat balance of the cell must be such that the molten electrolyte largely is contained—save for the underlying molten metal pool on which it is supported—within a skull of its own composition. This will be obvious from a consideration of the fact (1) that carbon cannot be used as a container because of contamination and the further fact (2) that no known ceramic material is inert in, or not attacked by, contact with fused fluorides and oxides. In practice, the proper heat balance is attained by (a) making the cell in the form of a wide dish, (b) by establishing and maintaining an electrolyte composition suitable (1) as to MnO solubility and (2) as to melting point (or, more properly, melting range) with respect to the melting point of the product metal and (3) as to its electrical conductivity. Thus, the fused electrolyte must contain sufficient oxides to prevent high voltage “anode effects,” and must be capable of dissolving sufficient MnO that manganese is preferentially electrolyzed at the cathode.

Again, and apart from temperature influence, a suitable solubility of MnO (in the bath) depends upon the proper combination of oxides in the bath composition, the presence of oxides having acid characteristics apparently being essential—or, at least, very desirable—for practical cell operation.

As regards the melting point (or range) of the fused electrolyte, practical operation dictates that the melting point cannot be appreciably lower than that of the product metal, since otherwise a suitable flux skull cannot be maintained around the fused pool of electrolyte: its melting point should not be more than 100° or at most 150° C. below the melting point of the product metal.

On the other hand, from the standpoints of electrical conductivity and fluidity it is essential that the fused electrolyte contain a substantial amount—at least 50% by weight—of a fluoride, and economic as well as melting point evaluation singles out CaF₂ as being the commercially most important, if not the only practical fluoride. It is noted, in this connection, that the electrical resistance

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of fused oxides—including MnO—is some 20 times that of CaF_2 with dissolved MnO in it. While it is possible to operate the cell with an electrolyte below 50% in CaF_2 and high in Al_2O_3 if the cost of electricity were unimportant, it appears that a CaF_2 percentage below 55–60% is generally impractical because of the relatively low conductivity of the fused electrolyte.

As regards electrical operation, the cell may be operated at anode current densities as high as 10,000 amps./sq. ft. or higher; or, as low as may be necessary to maintain a temperature level suitable for maintaining the electrolyte (and pool of product metal) freely fluid; in commercial operation, the "normal" anode current density is within the range 1,000–3,000 amps./sq. ft. The cathode current density is not critical. The operating voltage of the cell normally falls within the range 5.0–6.5 volts—lower voltages being consistent with larger cell units.

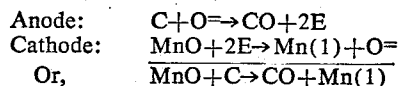
The carbonaceous anode may be formed from coal carbon, graphite, or—preferably—petroleum coke carbon, e.g. Soderburg anodes made from petroleum coke carbon. Use of this latter material is indicated in the event a very high purity product is desired.

The intermittent step of tapping molten manganese from the maintained cathodic pool thereof may be effected by conventional oxygen lancing as practiced in blast furnace operation: preferably, however, it is effected by electrically melting a metal rod insert provided, for this purpose, in an aperture or tapping port in the aforesaid layer of inert refractory oxide on which the pool of molten product metal is supported, allowing a desired portion (less than all) of the molten product metal to flow out of the pool through the thus-opened aperture, and then re-sealing the tapping aperture by inserting a cold (fresh) metal rod insert into said aperture. The melting of the metal (e.g. iron, or mild steel) rod insert is effected by passing a high current (either A.C. or D.C.) through the rod. This tapping method is superior to lancing because it is precise, easily carried out, and results in almost no deterioration of the tapping port.

The product metal, as tapped from the cell, is characterized by a very low concentration of carbon, values as low as 0.06–0.05% carbon having been attained in actual practice, whilst the contents of other impurities—not purposely added as alloying components—depend upon the purity of the feed (i.e., upon the purity of the MnO—containing material added to the fused oxide-fluoride bath). Manganese metal assaying over 99.0% Mn readily can be produced by the carrying out of this process, the customary "impurities"—over and above an exceedingly small amount of carbon—being iron and silicon.

ELECTROCHEMISTRY OF PROCESS

The electrochemistry of the process of the present invention has a superficial similarity to that of the Hall process of reducing aluminum, the chemical equations representing the over-all cell reaction being expressible simply as follows:



Moreover, both in the Hall process and in the present process the basic purpose of the fused electrolyte is to supply an electrically conductive solvent for the oxide of the product metal. But here the similarities stop, because the chemistry within the fused electrolyte is markedly different.

The solubility of MnO in the fused electrolyte of this process is largely the result of compound formation between the MnO and the acid oxides present in the fused electrolyte. It is intended that none of the Mn is in di-

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rect combination with fluorine. The compound formation of MnO with the acid oxides is an essential feature of the process, since it sufficiently inactivates the MnO to prevent it from directly reacting with carbon. If this were not the case a reaction would occur between the MnO and stray non-anodic carbon to form objectionable quantities of high carbon metal in the product. The acid oxides are equally important in facilitating the rapid and positive solution of MnO.

Amongst operable oxides with acid characteristics are B_2O_3 (e.g. in the form of borax glass $\text{Na}_2\text{OB}_4\text{O}_6$ or borax), Al_2O_3 , TiO_2 , SiO_2 or a combination of these or similar oxides.

It is believed that the chemistry involved at the cathode can be resolved into an evaluation of the stabilities of the various oxides. Any alkali or alkaline earth metals present in the fused electrolyte, if cathodically reduced, will displace all of the metals under consideration by virtue of their electromotive force. If it be assumed, then, that it is unimportant whether or not sodium, calcium or magnesium may be an intermediate in the cathode reaction, the selectivity of the cathode discharge reaction can be evaluated on the basis of the free energy of formation of the various oxides that may be present, as follows:

Thus, the generalized reaction of manganese metal with the respective oxide may be set up as a basis of comparison:



Then the table below can be developed:

Oxide:	ΔF of reaction at 1327° C. in kcal.
Al_2O_3	+86.8
B_2O_3	+24.0
SiO_2	+14.9
TiO	+14.6
V_2O_3	+9.7
MnO	0
Cr_2O_3	−18.3
FeO	−25.0
CoO	−35.9
Cu_2O	−49.4
MoO_2	−50.2
WO_3	−83.4
NiO	−105.1
(CO)	−3.2)

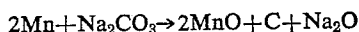
This indicates that Ni, W, Mo, Cu, Co, Fe and Cr will be displaced in preference to Mn in that order, while V, Ti, Si, B and Al will be displaced after Mn with increasing difficulty as listed. The value of CO is indicated to show that the over-all cell reaction for manganese should proceed at a very low theoretical voltage.

However, inasmuch as one is concerned with compound formation in the fused electrolyte, the values in the above table may be shifted somewhat depending upon the stability of the compound formed. Thus, the stability of MnO is significantly increased by the formation of $\text{MnO} \cdot \text{B}_2\text{O}_3$.

It is important to note that B_2O_3 is sufficiently more stable than MnO (+24 kcal.) that boron is not electrolyzed until the manganese level is very low or in the event of extremely high cathode current densities. Silicon with a free energy value of +15 kcal., on the other hand, represents more of a problem. In order to avoid excessive silicon in the product, as SiO_2 builds up in the fused electrolyte from the ore feed, it is essential that the current density be kept reasonably low or if a particularly high silica ore is involved it may be necessary to include in the feed a compound which will increase the SiO_2 stability, CaO , Al_2O_3 or MgO for example.

It has been found that the value of the electrolyte composition is depreciated by the presence therein of

substantial concentrations of alkalis, particularly, alkali carbonates. The alkalis tend to lower the melting range of the electrolyte composition to a critical range, and moreover, the alkali carbonates tend to react with metallic manganese according to the equation



which reaction results in the undesirable addition of carbon.

It has been found, further, that the reduction of SiO_2 to elemental silicon should be prevented by "tying up" the silica in the form of a silicate. In this connection, it has been discovered that excess CaO in the electrolyte composition tends to form, with the SiO_2 content, an eutectic having an undesirably low melting point, but that "tying" the SiO_2 with Al_2O_3 is much more advantageous.

CELL FEED

The cell feed varies widely depending upon the metal or alloy being produced and also in terms of compensating adjustment in the fused electrolyte to correct for impurities inherent in ores of lower grade. Several cases are discussed below which demonstrate the flexibility of the system.

(A) Two special cases exist in which, for all practical purposes, the fused electrolyte maintains a constant composition over long periods of operation.

(1) Where the feed is a high purity metal oxide, MnO , for example.

(2) Where the feed is in the form of a metallic anode bar.

A combination of these two special cases represents a practical system for the production of special alloys. For example high purity MnO can be electrolyzed using a carbon anode while an anode bar of Cu or Ni is simultaneously fed into the cell at a controlled rate to produce a Cu-Mn or Ni-Mn alloy of any desired composition.

(B) When the ore feed is impure, contaminating impurities build up in the fused electrolyte. Depending upon the nature of the impurities, the effect may be to raise the melting point and viscosity as well as the electrical resistance (this being true of a high Al_2O_3 contamination); or, the effect may be to lower the melting point below a practical limit, which latter might result from a very high alkali content or certain combinations of CaO and SiO_2 and/or Al_2O_3 and SiO_2 . In either event it is necessary to feed CaF_2 (sometimes borate) along with the ore, and to tap off the excess electrolyte thereby produced, so that the fused electrolyte is maintained within a practical operating composition. Below 50% CaF_2 is normally considered impractical.

(C) Certain alloys involve metals which cannot be practically fed as anodic rods, boron for example, in which case the feed is made to include the alloying oxides blended in the proper proportion to give the desired alloy.

In a consideration of the cell feed, it is to be noted that the inclusion therein of significant amounts of higher valence manganese—e.g. a poorly reduced MnO_2 ore characterized by a high percentage of Mn_3O_4 —obviously leads to inefficient current utilization, i.e., the necessity of more electrons passed per unit of manganese produced, and, therefore, is to be avoided.

The invention will now be described in further detail in the following examples, and the apparatus aspect thereof described with reference to the accompanying drawings, in which latter

FIGURE 1 is a diagrammatic view, in vertical cross-section with certain parts removed, of a pilot cell operable in the carrying out of the present process;

FIGURE 2 is a diagrammatic view, in vertical cross-section, of a modified form of the cell represented in FIGURE 1;

FIGURE 3 is a generalized detailed view, in longitudinal vertical cross-section, with certain parts removed, of a commercial-sized cell;

FIGURE 4 is a generalized detailed view, in transverse vertical cross-section of the cell shown in FIGURE 3, and

FIGURE 5 is a ternary diagram of the system $\text{CaF}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$, showing in cross-hatched area the range of composition of electrolyte in which the process of the present invention can be carried out.

Referring, first, to FIG. 5, it is to be noted that the line A—B represents the composition $\text{Al}_2\text{O}_3\text{-SiO}_2$ below which composition, with respect to alumina, silicon will be electrolyzed. Line B—C represents a temperature boundary set at about 1200°C . Area D represents a limited range, below the composition $\text{Al}_2\text{O}_3\text{-SiO}_2$ in which the excess SiO_2 can be chemically combined with CaO and still maintain adequate melting point.

In FIGURE 1, a relatively shallow vessel 1 of steel constitutes the outer supporting shell of the cell, the vessel being lined—both as regards its walls and its bottom—with heat-insulating ceramic material 2.

Overlying the bottom insulation is a generally impermeable layer 3 of a refractory ceramic material—such for example as alumina or magnesia brick or their respective ramming mixtures which is inert to molten manganese. There is embedded in layer 3 an electrically conductive metal cathode contact bar 4 at least the upper surface of that part of the bar which is within the shell of the cell being at a height at least as great as is the upper surface of layer 3 so as to be exposed thereabove. Contact bar 4, which extends outwardly from the cell may be formed of any suitable electrically conductive metal, unless a very small amount of iron alloying is intolerable during the initial stages of cell operation. It is to be understood that after an extended period of operation the cathode contact bars will no longer alloy into the product metal. It is preferred that contact bar 4 be formed of iron or steel. At any suitable locus adjacent the central portion of layer 3 there is fabricated a tapping port 5 formed of high-alumina sintered shapes defining a generally cylindrical tapping aperture 5' normally closed (or "sealed") by an iron rod 6.

Above layer 3 and extending about the inner periphery of lining 2 is a back-up wall 7 of "dish" configuration. This back-up wall is, during use of the apparatus, in contact with a pool of molten metal—indicated at 8—supported on layer 3, and also with a mass of electrolyte composition 9, 9' (about to be described) the most nearly central part of which latter may, on occasion, be molten; consequently, the back-up wall 7 is formed of a material, e.g. high-alumina brick, which is suitably inert both to molten product metal and to the fused electrolyte composition.

The parts described above—together with the anode member and confining hood later to be described—constitute the invariant portions of the operating cell. The shallow "dish" formed by layer 3 and the sloping sides of back-up wall 7 constitute the receptacle for (a) a pool 8 of molten manganese (product metal) lying upon layer 3 and—overlying said pool—a mass of electrolyte composition 9, 9'. The central and lower portions of the mass of electrolyte composition, indicated at 9, are normally molten, whereas the more outlying portions of said mass, indicated at 9', are normally solidified (i.e., "frozen") and constitute the solid, bath-confining skull referred to hereinabove.

A generally cylindrical and vertically disposed hood member 10 is supported (by any suitable means, not shown) centrally above the above-described shallow

"dish" and is so disposed that the lower edge 10' of the hood member is embedded and sealed in the solid skull mass 9'. A suitable feed orifice 11 is provided in an upper part of the hood member (either at the top thereof, as shown, or in the upper part of the side wall of the hood member above the upper extremity of the skull mass 9'), which feed orifice normally is closed by a door 12. Centrally disposed in the top of hood member 10 is a relatively large anode orifice 13 through which latter a massive anode bar 15 extends so that its lower end is immersed in molten electrolyte 9. The annular space between anode member and anode orifice may, if desired, be substantially sealed by the interposition of an annular gas sealing means (not shown). The purpose of hood member 10 is to maintain a small positive pressure of reducing gas—consisting largely of carbon monoxide—about the un-immersed but hotter part of anode whereby to protect the anode from oxidation.

The means for supporting anode bar 15, and for adjusting the distance between the lower end of anode bar 15 and the cathodic pool 8 of product metal, being conventional, are not shown. At its upper end, anode bar 15 is electrically connected to a conventional anode bus 16.

In a similar manner, contact bar 4 is electrically connected to a conventional cathode bus 17.

Not shown in the drawing, there is provided, above the entire cell, a suction hood of conventional design for positive upward displacement of by-product gases by an enveloping current of fresh air.

In use, a particulate mixture of electrolyte composition components is placed in the aforesaid shallow "dish" and melted therein by the passage of current from the anode to the cathode contact bar. As soon as a molten bath begins to form, the feed of manganese oxide begins whereby to establish a cathodic pool of molten manganese underlying the flux bath and overlying said cathode contact bar. Thereafter, the feed of MnO to the molten electrolyte continues, with or without the simultaneous or intermittent feeding in of additional particulate electrolyte components as needed. Continuance of the operation results in the building up of a skull of electrolyte about (i.e., around and above) a central body of molten electrolyte. The manganese oxide is dissolved by the molten electrolyte, and manganese in molten form is deposited at the cathode, thereby progressively increasing the volume of the cathodic pool. When the volume of molten manganese reaches a predetermined value, the sealing means is removed from the tapping orifice, and a suitable portion of the molten product metal is allowed to flow out of the cell into an ingot mold. Thereupon, the tapping orifice is sealed shut by introducing a cold rod into it, whilst the operation of the cell continues.

In the event the volume of electrolyte in the cell becomes excessive, it is diminished to the desired level, e.g., by opening a flux orifice in the skull and allowing an appropriate amount of molten electrolyte to flow out.

According to FIGURE 2, the contour of the aforesaid shallow "dish" may be modified to provide therein a centrally disposed well 21, lined with high-alumina brick, adapted to contain all or substantially all of the cathodic pool of molten product metal. Also, the side walls of the metallic outer shell 1 of the cell are extended upwardly, well above the upper level of the electrolyte skull, and are bridged by a cover member 1'. In this embodiment the carbon anode 15' is suspended within the cell from a conductive metal shaft 22 which latter is electrically connected to an anode bus and extends into the cell through a central opening 13' in cover 1'.

FIGURES 3 and 4 illustrate essential elements of a cell for use in a full-scale commercial operation of the process. In these figures the cathodic pool of molten product

metal and the electrolyte have not been shown, it being understandable that during use of the apparatus a "frozen" skull of electrolyte composition would form and persist about a centrally disposed pool of molten electrolyte composition and would extend upwardly from and inwardly over, said pool to seal the lower portion of the hood 10, and simultaneously a pool of molten product metal would form and persist underneath the electrolyte and in contact with the cathode contact bar 4.

In the embodiment illustrated in FIGURES 3 and 4, that part, 31, of the aforesaid shallow "dish" which is intended, in use, to contact electrolyte is formed of high-alumina brick, whilst the part, 32, intended to be contacted only by molten product metal is formed of corundal ramming mix. Both the alumina brick and the corundal ramming mix layer overlie and are backed-up by a layer, 33, of carbon brick. A mass, 34, of heat-insulating masonry underlies and supports the above-described layers. A feed screw member 36 is disposed in feed orifice 11 for feeding manganese oxide onto the electrolyte.

At 37 is schematically shown a contact member, projecting into anode bar 15, for conducting electrical current from anode bus 16 to the anode bar.

SPECIFIC EXAMPLES

Example 1

The apparatus used was that illustrated in FIGURE 2: the upper portion of the cell containing the fused electrolyte was one foot square, and the molten manganese pool was 3 inches square in horizontal cross-section.

The cell was brought up to operating temperature and to temperature equilibrium by passing an alternating current through a fused CaF_2 electrolyte, a carbon rod acting as one electrode and a manganese melt acting as the other electrode. An initial charge of 500 grams of manganese metal had been added to establish the metal electrode (cathode).

After temperature equilibrium had been established, sufficient $\text{Na}_2\text{B}_4\text{O}_7$ and MnO were added to the fused CaF_2 to give a fused electrolyte containing 10 parts CaF_2 to 1 part $\text{Na}_2\text{B}_4\text{O}_7$ to 2 parts MnO. The A.C. current was then disconnected and D.C. current passed as indicated in FIGURE 2. During D.C. operation 130 grams of MnO were fed every 15 minutes. It was necessary, however, because of the high heat loss from such a small cell occasionally to change from D.C. to A.C. current in order to raise the temperature to the desired level.

The pertinent data are summarized below:

Total D.C. amp. hours.....	2525.
Metal produced by electrolysis..	2060 gms.
Current efficiency.....	75%.
Average D.C. current.....	400 amps.
Average anode current density..	10,000–14,000 amps./ft. ² .

Metal analysis:

Mn—	94.0%.
Fe—	4.2%.
C—	0.12%.
Balance—	Al, Si and traces of other metals.

Example 2

The cell used for this experiment was identical in general design to that shown in FIGURE 1. The anode was 20 inches in diameter and made from carbon. The overall dimensions of the cell itself were 6' x 10' in horizontal cross-section.

The log of the entire run is shown below:

At this point, some alloying of the iron of the cathode

HIGH PURITY MnO FEED

Date	Avg. volts	Avg. Kva	Lbs. of Mn fed as MnO	Percent Mn in fused electrolyte	Percent Fe ₂ O ₃ in fused electrolyte	Analysis of metal product				Lbs. of metal tapped	Comments
						Mn	Fe	C	Si		
9-28-----	8.7	45.7	270	6.1	2.2	88.4	10.0	.21	-----	117	Melting out tapping port electrically.
9-29-----	8.6	44.3	248	6.9	2.0	91.7	10.0	.24	-----	230	Do.
9-30-----	8.7	45.9	250	7.3	2.3	94.5	4.2	.16	-----	135	Do.
10-1-----	8.5	46.1	255	5.8	1.6	94.9	3.8	.15	.76	150	Do.
10-2-----	8.5	46.1	289	6.0	2.7	-----	3.6	.15	-----	255	Do.
10-3-----	8.6	46.5	293	5.7	3.0	-----	2.7	.15	-----	150	Do.
10-4-----	8.7	48.8	302	5.8	-----	-----	-----	.11	-----	280	Lanced.
10-5-----	8.7	49.4	315	6.2	2.8	97.9	1.9	.11	-----	425	Do.
10-6-----	8.8	49.8	313	5.5	2.8	97.7	1.5	.14	-----	235	Do.
10-6-----	8.8	49.8	313	5.5	2.8	97.9	1.8	.12	.14	235	Do.

(REDUCED) NATURAL ORE FEED

10-7-----	9.0	48.8	255	7.5	3.2	97.4	2.1	.15	-----	285	Lanced.
10-8-----	8.7	47.0	196	7.3	-----	95.1	4.4	.17	.75	250	Melted out tapping port electrically.
10-9-----	8.7	45.4	225	6.5	-----	91.6	6.4	.15	2.0	175	Do.
10-10-----	8.8	44.5	235	8.2	-----	89.7	7.9	.14	2.5	125	Do.
10-11-----	8.8	44.9	48	9.2	-----	89.3	8.0	.13	2.8	233	Used up anode.
10-11-----	8.8	44.9	48	9.2	-----	-----	-----	.12	-----	-----	-----

¹ The high iron percentage in the initial taps was due to the fact that the mild steel cathode contact bars were alloying into the metal product.

Additional pertinent data calculated from the above log were as follows:

Average anode current density----- amps./ft.²----- 2500 30
 Average current efficiency (correcting for higher valence manganese and also the contained iron and silicon)----- percent----- 93.5
 Carbon (anode) efficiency based on CO evolution----- do----- 96.5 35

The analysis of the natural ore before reduction fed during the latter part of the run was as follows:

Percent
 Mn ----- 52.1 40
 Fe ----- 5.7
 SiO₂ ----- 7.8
 Al₂O₃ ----- .3

It might be noted that the silicon electrolyzed during the ore feed portion of the run was high because of a combination of two factors: (1) high current density, 45 and (2) Al₂O₃ and/or CaO were not present in sufficient quantity to inactivate the SiO₂ by chemical combination. When electrodes of 30" diameter are employed the current density drops to less than 1500 amps./ft.² and the electrolysis of silicon is substantially reduced. 50

Example 3

The following log shows the data obtained from a 35 day run of an experimental cell having a 20" anode and a 6' x 10' external shell. 55

The operation was started by striking an arc between a carbon anode and solid Mn, lying on an embedded iron cathode contact bar, and covered with a mass of powdered CaF₂. As Mn and CaF₂ melted, additional CaF₂ 60 was added to build up a skull surrounding a pool of molten fluorite overlying a pool of molten Mn.

contact bar with the Mn of the cathode pool took place.

The size of the CaF₂ pool increased to a diameter somewhat in excess of the diameter of the carbon anode, this pool being contained within a solid skull which formed about and above the liquid—roughly, a vessel with a necked-in mouth at the top.

This initial procedure was continued until the cell had reached temperature equilibrium and a pool of sufficient size had been formed. Then, MnO (reduced ore) was added to the CaF₂ pool along with another oxide, such as Al₂O₃ or SiO₂ or an oxide of boron, to increase the solubility of MnO in the electrolyte and to increase the O₂ content of the fused electrolyte in order to prevent anode passivity or "anode effects."

This start-up procedure applies not only to this particular example but also to Example 2 and to the start-up of a multi-anode commercial cell.

At this stage, the passage of A.C. current was interrupted and passage of D.C. current between the carbon anode and the cathode pool was initiated. Thereafter, reduced ore was fed into the pool of molten electrolyte in proportion to the D.C. current. The reduced ore contained about 2.75% Al₂O₃ and 1.4% SiO₂ and about 2.1% iron as Fe₃O₄, about 1.9% potassium oxide and balance essentially all MnO.

The voltage imposed between the electrodes was maintained at a uniform level between 7 and 7.5 volts. Also the D.C. current was held as nearly uniform as possible. The approximate resistance of the fused electrolyte at any particular stage of operation was therefore an inverse function of the anode-cathode separation. The experimental run was divided into 3 parts, indicated as A, B and C in order to demonstrate various properties of the electro-chemical system and each part will be analyzed separately.

LOG OF EXPERIMENTAL CELL RUN NO.

Days of operation	Anode-cathode separation (")	D.C. amps	Pounds Mn fed as MnO in ore	Percent Mn in fused electrolyte	Percent Fe ₂ O ₃ in fused electrolyte	Percent CaF ₂ in fused electrolyte	Mn in product	Fe in product	C in product	Si in product	Pounds metal tapped	Flux temp. of—	Remarks
A													
1-----	4	4,290	143	10.0	0	90	-----	-----	-----	-----	-----	-----	
2-----	4	4,080	153	7.9	0	80	81.3	15.4	.46	1.98	35	2,290	
3-----	4	4,560	234	7.9	0	73	81.7	15.3	.40	2.02	170	2,360	
4-----	3	4,520	244	9.4	0	65	84.7	12.7	.33	1.66	220	2,340	
5-----	2	4,610	222	7.8	0	55	87.5	10.2	.27	1.46	180	2,350	Solid phase forming.
6-----	<1	4,690	240	6.2	0	53	89.5	8.0	.20	1.34	330	2,340	Solid phase present.
7-----	<1	4,660	231	5.1	0	50	91.4	7.0	.17	1.04	305	2,315	Do.
8-----	<1	4,550	272	5.1	0	56	92.6	6.0	.16	.84	295	-----	Do.

LOG OF EXPERIMENTAL CELL RUN NO.—Continued

Days of operation	Anode-cathode separation (")	D.C. amps	Pounds Mn fed as MnO in ore	Percent Mn in fused electrolyte	Percent B_2O_3 in fused electrolyte	Percent CaF_2 in fused electrolyte	Mn in product	Fe in product	C in product	Si in product	Pounds metal tapped	Flux temp. of—	Remarks
9-----	<1	4,690	273	5.6	0	60	92.1	6.7	.16	.10	180	2,310	Solid phase present. Solid phase disappearing—Borate added.
10-----	3	4,450	262	6.1	2.0	65	93.4	6.0	.15	.009	160	2,290	
11-----	3	4,860	251	6.8	1.6	60	94.0	5.4	.15	.006	200	2,330	
12-----	3	4,900	295	6.1	1.2	63	94.1	5.0	.14	.013	170	2,350	
13-----	3	5,030	294	7.2	-----	62	94.8	4.0	.14	.065	220	2,310	
14-----	3	4,920	290	8.7	-----	60	94.1	4.2	-----	.01	220	2,340	
15-----	3	5,140	242	8.6	1.0	60	95.1	3.3	-----	.12	140	2,310	
16-----	3	5,410	250	7.7	-----	58	95.2	3.0	-----	.23	250	2,270	
17-----	3	5,430	266	7.3	-----	60	94.8	3.2	-----	.15	285	2,270	
B-----													
18-----	3	5,530	139	6.3	-----	60	-----	-----	-----	-----	30	2,200	Metal freezing adding lime. Adding lime. Metal frozen adding lime. Do. Metal frozen.
19-----	2	4,920	71	1.3	0.2	60	-----	-----	-----	-----	-----	2,140	
20-----	2	5,200	259	2.9	0.1	60	-----	-----	-----	-----	-----	2,240	
21-----	2	5,530	270	-----	0.2	60	-----	-----	-----	-----	-----	2,220	
22-----	2	5,100	-----	2.4	-----	60	-----	-----	-----	-----	-----	2,130	
C-----													
27-----	4	5,670	120	0.5	0.9	90	-----	-----	-----	-----	380	2,300	Metal frozen. Do. Do.
28-----	4	4,430	166	3.0	1.6	80	-----	-----	-----	-----	455	2,300	
29-----	4	4,380	263	5.9	3.5	75	-----	-----	-----	-----	285	2,290	
30-----	3.5	4,910	279	5.7	3.0	70	-----	-----	-----	-----	275	2,270	
31-----	3	5,300	288	6.1	2.5	60	-----	-----	-----	-----	175	2,320	
32-----	3	5,100	306	6.9	2.4	60	-----	-----	-----	-----	300	2,280	
33-----	<1	5,170	299	8.2	2.6	40	-----	-----	-----	-----	280	2,250	
34-----	<1	5,430	291	9.2	-----	45	-----	-----	-----	-----	-----	2,260	
35-----	<1	5,530	132	7.3	2.0	50	-----	-----	-----	-----	-----	2,260	

Part A.—This portion of the experimental run demonstrates (1) the control of silicon in the product by causing the SiO_2 in the fused electrolyte to form a stable compound with alumina and thus preventing its electrolysis, and (2) the elimination of objectionable solid phases in the fused electrolyte by the addition of sodium borate.

The control of silicon is demonstrated by the fact that the fused electrolyte initially contained an excess of 50 pounds of SiO_2 while the ore feed contained alumina and silica in the amounts of 2.75% Al_2O_3 and 1.4% SiO_2 . The log shows that the silicon in the product metal started at about 2%, dropped slowly to about 1% and then suddenly fell to 0.1%. Calculations of the Al_2O_3 to SiO_2 ratio at this point show it to be one to one molar, indicating that the electrolysis of silicon essentially stopped as soon as the excess SiO_2 over the compound $Al_2O_3 \cdot SiO_2$ was removed from the fused electrolyte.

The log also shows under "remarks" that solid phases developed in the fused electrolyte, presumably from high melting silicates. The presence of this solid non-conductive material in the fused electrolyte raised its electrical resistance as is evidenced in the low anode-cathode separation. The log shows that the solid phases as well as the high resistance were eliminated by the addition of some 2% borate. With borate added as needed the cell continued to operate satisfactorily in all respects.

It should be noted also for comparison in part C that satisfactory operation was observed when the CaF_2 level in the fused electrolyte was held at 60%.

Part B.—This portion of the run demonstrates the adverse effect of adding excessive CaO to the fused electrolyte. Two difficulties resulted as demonstrated by the log: (1) the basic character of the CaO markedly decreased the solubility of the MnO , and (2) the melting point of the fused electrolyte was dropped sufficiently to make it impossible to maintain the product pool in a molten condition. The depression of the melting point was due to the formation of an eutectic mixture of CaF_2 and $CaO \cdot SiO_2$.

Part C.—This portion of the run demonstrates the difficulty in operation as a result of a low CaF_2 concentration.

The log shows satisfactory cell operation as the CaF_2 percentage is dropped from 90% down to 60%. At 40% CaF_2 however, two adverse electrical effects are evident: (1) the resistance of the fused electrolyte is high in spite of the fact that no solid phases were present, and (2) the melting point of the fused electrolyte was too low to maintain a molten product pool. (See FIG. 5, showing the low melting eutectic area of the three phase system $Al_2O_3-SiO_2-CaF_2$.)

In general, a small content of iron in the low-carbon product metal is tolerable. In cases, however, where it is essential that the product metal be substantially devoid of iron, other heavy metals, and phosphorus, the process of the present invention advantageously is supplemented as follows:

As the feed to the cell, we provide a synthetic composition which is a slag product of a furnace operation wherein ferromanganese is produced, said slag consisting essentially of MnO , 60–80% by weight, and the balance consisting essentially of CaF_2 plus Al_2O_3 plus SiO_2 , the combined weight of Al_2O_3 and SiO_2 to the weight of CaF_2 being in the ratio of about 2:3.

In preparing this synthetic feed an electric arc furnace is fed with natural manganese ore (e.g., pyrolusite) and sufficient carbon to reduce all of the MnO_2 of the ore to MnO plus sufficient additional carbon to reduce a portion (e.g., 20%) of the total manganese in the ore to metallic Mn, together with CaF_2 in an amount sufficient to meet the above ratio balancing the Al_2O_3 and SiO_2 contents of the ore. In this operation, substantially all of the heavy metals other than manganese, including iron, in the ore are metallized and all sources of carbon as carbonates and of phosphorus are removed from the slag. The ferro-manganese product of this electric furnace operation is, necessarily, adulterated with carbon, phosphorus and such heavy metals as may have been present in the ore, whereas the slag has been substantially purified with regard to the elements just mentioned. The ferro-manganese and the slag are separately tapped off, and the slag is cooled and then crushed to a fineness suitable for feeding to the electrolytic cell.

By resorting to the use of this synthetic feed, the metal product of the electrolytic process is extremely pure not only as regards carbon and silicon contents but also essentially devoid of phosphorus, iron and other heavy metals.

Example 4.—Mn—Cu alloy

(A) Cu—Mn alloy consisting of 70% Mn and 30% Cu was prepared in the same physical cell as described in Example 3. The starting procedure described in Example 3 was followed with the exception that the manganese oxide was solubilized with borate instead of SiO_2 . After the cell was stabilized on D.C. current an additional anode—connected to the common anode bus—consisting of a copper bar was lowered adjacent to the carbon anode and anodically solubilized in the electrolyte. The rate of addition of Cu was controlled by the rate of which the copper bar was lowered into the pool, and the ratio of Cu added per unit of time to the Mn added during the equivalent period was maintained at 3:7. The

D.C. current was maintained at an average value of 5,000 amp., and the cumulative feed of Mn and Cu was controlled by the percentage of Mn in the fused electrolyte: average, 6%. The MnO feed was in the form of high-purity MnO (from MnCO_3). The bath temperature during the run was maintained at about 2300° F.

The product was tapped in the conventional manner, and upon analysis was found to consist—save for incidental impurities—of Mn and Cu, in the proportion of 70:30.

Example 5

In a repetition of Example 4, the copper bar is replaced by a bar of nickel and the current is increased to 5,500 amps., the other conditions of operation remaining the same. The nickel bar is lowered at a rate to establish and maintain a 1:1 ratio with the Mn added by way of the feed. The control of the cumulative feed of Mn and Ni is controlled by the percentage of Mn in the fused electrolyte being maintained at an average of about 6%.

The product metal consists, except for incidental impurities, of Mn and nickel in the ratio of 1:1.

Example 6

In this experiment a Mn-B alloy, containing about 5% B, was produced by the above-described process.

The cell was started by the initial feeding of CaF_2 and Al_2O_3 (in ratio of 85:15), whereupon sodium borate and high-purity MnO were fed in amounts to provide a Mn-to-B ratio of 95-5. After an initial period of operation, the sodium borate was substituted by B_2O_3 . The current was 5,000 amp., and the temperature of the bath was approximately 2300° F.

The cumulative feed was balanced against the D.C. current, with the assumption that the valence charge of manganese in the electrolyte process was 2 and that of the boron was 3.

The metal product, after tapping from the cell, was found to consist essentially of Mn and B, the content of B being 4-5%.

In a manner similar to that of Examples 4, 5 and 6 above, various 2-component alloys of manganese can be produced at operating temperatures up to about 1300° C., by simply changing the identity of the feed and the feed ratio. A number of such alloys so produced are indicated in the following table:

Mn—Sb	-----	All proportions.
Mn—As	-----	All proportions. ¹
Mn—Cr	-----	Cr range 0-20%.
Mn—Co	-----	Co range 0-75%.
Mn—Cu	-----	All proportions.
Mn—Fe	-----	Fe range 0-60%.
Mn—Ni	-----	Ni range 0-80%.
Mn—Si	-----	Si range 0->50%.
Mn—Sn	-----	All proportions.
Mn—Zn	-----	All proportions. ¹

¹ Consistent with boiling point of alloy.

We claim:

1. A fused salt electrolytic cell for the production of Mn, comprising a vessel open at the top and composed of side walls of fused Al_2O_3 or MgO and a bottom of a non-carbonaceous refractory material non-reactive with Mn, said bottom being configured and adapted to support a pool of molten Mn thereon, a cathode bus, a metallic conductor bar embedded in said bottom and extending inwardly to the bottom of said pool space and outwardly connected to said cathode bus, a metallic rod embedded in said bottom and extending inwardly to said pool space, a hood member supported above said vessel and having a top opening, a carbon anode extending substantially vertically into said vessel and terminating above and adjacent said pool space, a feed orifice in said hood, a peripheral body of solidified electrolyte covering said side walls and extending inwardly and upwardly into proximity

with said anode and into sealing relation with the bottom of said hood, said peripheral body constituting the side walls of an electrolyte space whose bottom wall is the top of said metal pool, an anode bus, and an electrical conductor connecting said anode bus with said anode.

2. A fused salt electrolytic cell for the production of Mn, comprising a vessel open at the top and composed of side walls of fused Al_2O_3 or MgO and a bottom of a non-carbonaceous refractory material non-reactive with Mn, said bottom being configured and adapted to support a pool of molten Mn thereon, a cathode bus, a metallic conductor bar embedded in said bottom and extending inwardly to the bottom of said pool space and outwardly connected to said cathode bus, a metallic rod embedded in said bottom and extending inwardly to said pool space, a hood member supported above said vessel and having a top opening, a carbon anode member extending substantially vertically through said hood opening and into said vessel and terminating above and adjacent said pool space, a gas sealing means between said anode member and said hood opening for maintaining within said hood a reducing gas atmosphere, a feed orifice in said hood member, a peripheral body of solidified electrolyte covering said side walls and extending inwardly and upwardly into proximity with said anode member and into sealing relation with the bottom of said hood member, said peripheral body constituting the side walls of an electrolyte space whose bottom wall is the top of said metal pool, an anode bus, and an electrical conductor connecting said anode bus with said anode.

3. A process for the production of low-carbon, low-silicon manganese from a lower oxide of manganese, which comprises establishing a fused electrolytic bath consisting essentially of calcium fluoride, a lower oxide of manganese and a mixture of inorganic oxides including an acid-acting oxide whose free energy change of reaction with manganese at 1327° C. to form MnO is greater than zero, and a basic-acting oxide whose free energy change of reaction with manganese at 1327° C. to form MnO is greater than zero, said mixture of inorganic oxides having an overall acidic character sufficiently acidic to facilitate the dissolution of a lower oxide of manganese but having a sufficient alkaline content to prevent the substantial electrolysis of silicon, the fused bath containing from about 50% to about 90% by weight of calcium fluoride, and from about 0.5% to about 10% by weight of manganese as a lower oxide of manganese, and having a melting range of from about 1150° C. to about 1300° C., the bath composition being stable against decomposition and volatilization within said temperature range, confining said bath within a solid skull of its own composition above and contiguous to a pool of molten manganese, adding a material containing a manganese oxide to said bath, passing an electric current through said bath from an anode to the surface of said underlying pool of molten manganese as cathode, maintaining the bath at a temperature above the melting point of manganese and at such temperature, within said range, as to maintain molten at least the upper surface of said underlying pool of manganese, and intermittently tapping molten manganese from said pool, said process being further characterized in that said pool of molten manganese is supported on a carbon-free layer composed essentially of relatively electrically non-conductive refractory oxide which is non-reactive to manganese.

4. A process for the production of low-carbon, low-silicon manganese from a lower oxide of manganese, which comprises establishing a fused electrolytic bath consisting essentially of calcium fluoride, a lower oxide of manganese and a mixture of inorganic oxides including an acid-acting oxide of the group consisting of silicon dioxide and an oxide of boron and a basic acting oxide of the group consisting of alumina, calcium oxide, barium oxide, and magnesium oxide, said mixture of inorganic oxides having an overall acidic character sufficiently acidic

to facilitate the dissolution of a lower oxide of manganese but having a sufficient alkaline content to prevent the electrolysis of silicon, the fused bath containing at least 50% but not more than about 90% by weight of calcium fluoride and from 0.5% to 10% by weight of manganese as a lower oxide of manganese, and having a melting range of from 1150° C. to about 1300° C., the bath composition being stable against decomposition and volatilization within said temperature range, confining said bath within a solid skull of its own composition above and contiguous to a pool of molten manganese, adding a material containing a lower oxide of manganese to said bath, passing an electric current through said bath from an anode to the surface of said underlying pool of molten manganese as cathode, maintaining the bath at a temperature above the melting point of manganese and at such temperature, within said range, as to maintain molten at least the upper surface of said underlying pool of manganese, and intermittently tapping molten manganese from said pool, said process being further characterized in that said pool of molten manganese is supported on a carbon-free layer composed essentially of relatively electrically non-conductive refractory oxide which is non-reactive to manganese.

5. Process as defined in claim 3, said process being further characterized in that the layer which supports the molten manganese pool includes a solid conductive metal insert extending through said layer, and in that tapping molten metal from said pool is effected by electrically melting said metal insert.

6. Process as defined in claim 3, in which the content of CaF_2 in the bath is within the range of from about 60% to about 65% by wt. and the content of lower oxide of manganese in the bath is within the range of from about 4 to about 7% by wt.

7. A process for the production of low-carbon, low-silicon manganese from a lower oxide of manganese, which comprises establishing a fused electrolytic bath consisting essentially of calcium fluoride, a lower oxide of manganese and an oxide of boron, the content of manganese as lower oxide of manganese being from about 5.5 to about 15% by wt., the content of oxide of boron being from about 1.6 to about 8% by wt., the content of CaF_2 being the balance save for incidental impurities, said fused bath having a melting range of from about 1150° C. to about 1300° C., confining said bath within a solid skull of its own composition above and contiguous to a pool of molten manganese, adding a material containing a manganese oxide to said bath, passing an electric current through said bath from an anode to the surface of said underlying pool of molten manganese as cathode, maintaining the bath at a temperature above the melting point of manganese and at such temperature, within said range, as to maintain molten at least the upper surface of said underlying pool of manganese, and intermittently tapping molten manganese from said pool, said process being further characterized in that said pool of molten manganese is supported on a carbon-free layer composed essentially of relatively electrically non-conductive refractory oxide which is non-reactive to manganese.

8. Process as defined in claim 3, in which CaO is added to the bath as needed for minimizing electrolysis of silicon.

9. A fused salt electrolytic cell as defined in claim 1, in which the bottom of the cell is formed from a refractory oxide selected from the group consisting of MgO and Al_2O_3 .

10. In the process defined in claim 3, the improvement which consists in counteracting the formation of insoluble solid phases in the bath and promoting solution of MnO in the bath by the addition to the latter of an oxidic compound of boron in an effective amount of about 2% by weight based upon the total weight of the bath.

11. A process for the production of a low-carbon, low-silicon manganese alloy, which comprises establishing a fused electrolytic bath consisting essentially of calcium fluoride, a lower oxide of manganese and a mixture of inorganic oxides including an acid-acting oxide whose free energy change of reaction with manganese at 1327° C. to form MnO is greater than zero, and a basic-acting oxide whose free energy change of reaction with manganese at 1327° C. to form MnO is greater than zero, said mixture of inorganic oxides having an overall acidic character sufficiently acidic to facilitate the dissolution of a lower oxide of manganese but having a sufficient alkaline content to prevent the substantial electrolysis of silicon, the fused bath containing from about 50% to about 90% by weight of calcium fluoride, and from about 0.5% to about 10% by weight of manganese as a lower oxide of manganese, and having a melting range of from about 1150° C. to about 1300° C., the bath composition being stable against decomposition and volatilization within said temperature range, confining said bath within a solid skull of its own composition above and contiguous to a pool of molten manganese alloy, adding to said bath a material containing a manganese oxide and a source of alloying metal of the group consisting of heavy metals and oxides of heavy metals, passing an electric current through said bath from an anode to the surface of said underlying pool of molten manganese alloy as cathode, maintaining the bath at a temperature above the melting point of the manganese alloy and at such temperature, within said range, as to maintain molten at least the upper surface of said underlying pool of manganese alloy, and intermittently tapping molten manganese alloy from said pool, said process being further characterized in that said pool of molten manganese alloy is supported on a carbon-free layer composed essentially of relatively electrically non-conductive refractory oxide which is non-reactive to manganese alloy.

12. A process for the production of low-carbon, low-silicon manganese-boron alloy, which comprises establishing a fused electrolytic bath consisting essentially of calcium fluoride, a lower oxide of manganese and an oxide of boron, said fused bath having a melting range of from about 1150° C. to about 1300° C., confining said bath within a solid skull of its own composition above and contiguous to a pool of molten manganese-boron alloy, adding to said bath a material containing a manganese oxide and an oxide of boron, passing an electric current through said bath from an anode to the surface of said underlying pool of molten manganese-boron alloy as cathode to electrolyze said metals, maintaining the bath at a temperature above the melting point of the manganese-boron alloy and at such temperature within the aforesaid range as to maintain molten at least the upper surface of said underlying pool of manganese-boron alloy, and intermittently tapping molten manganese-boron alloy from said pool, said process being further characterized in that said pool of molten manganese-boron alloy is supported on a carbon-free layer composed essentially of relatively electrically non-conductive refractory oxide which is non-reactive to said manganese-boron alloy.

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