June 29, 1971 R. WINAND **3,589,988**

PROCESS FOR THE PRODUCTION OF CHROMIUM OF LOW CARBON CONTENT BY MEANS OF FUSED ELECTROLYTIC EXTRACTION AND CHROMIUM ALLOY OBTAINED THEREBY

Filed May 13, 1968 2 Sheets-Sheet 1

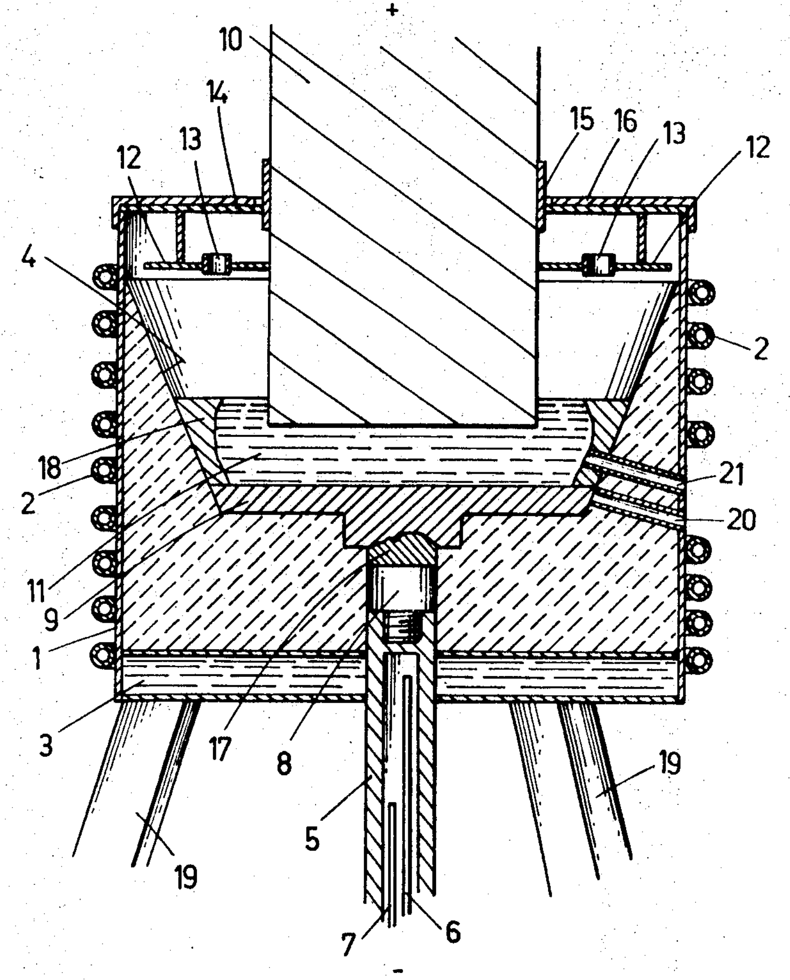

FIG.1.

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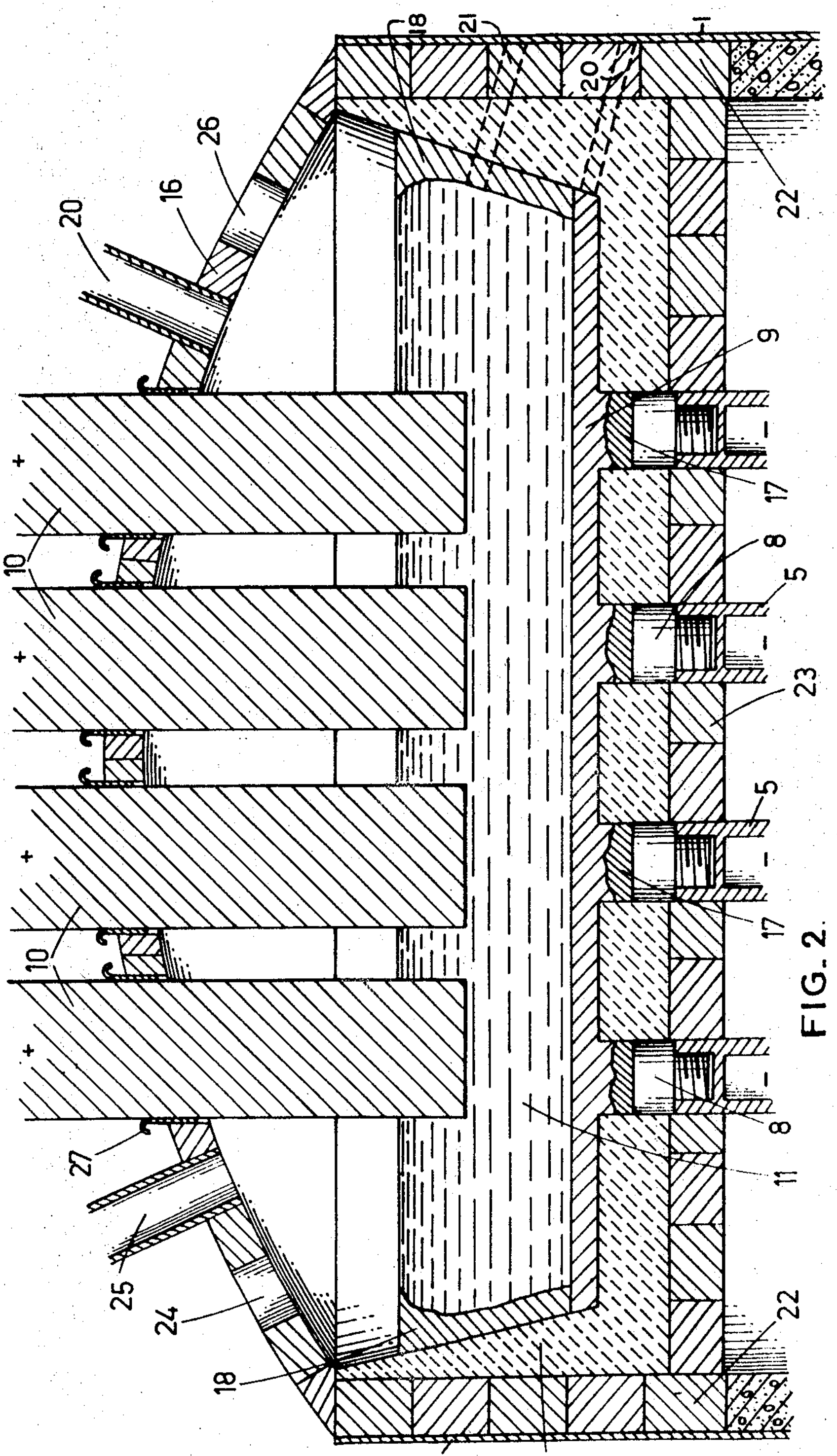

FIG. 2

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United States Patent Office

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3,589,988

PROCESS FOR THE PRODUCTION OF CHROMIUM OF LOW CARBON CONTENT BY MEANS OF FUSED ELECTROLYTIC EXTRACTION AND CHROMIUM ALLOY OBTAINED THEREBY

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Int. Cl. C22d *3/00, 3/20*
U.S. Cl. 204—64 **10 Claims**

ABSTRACT OF THE DISCLOSURE

A process and a cell are described for the production of chromium of low carbon content by means of fused electrolytic extraction, the said process including the use of an electrolytic bath deriving from a ternary system selected among the group comprising the systems the use of an electrolytic bath deriving from a ternary system selected among the group comprising the systems

$$Cr_2O_3\text{—}CaO\text{—}Al_2O_3,\ Cr_2O_3\text{—}MgO\text{—}Al_2O_3$$

$$Cr_2O_3\text{—}CaO\text{—}MgO,\ Cr_2O_3\text{—}SiO_2\text{—}CaO \text{ and}$$

$$Cr_2O_3\text{—}MgO\text{—}SiO$$

as well as the complex systems derived from compounds of the said ternary system, and the use of preference of a cathode provided by the metal to be extracted, such as the chromium or an alloy of chromium with another metal present in the electrolyte as an oxide.

The present invention relates to a process for the production of chormium of low carbon content by means of fused electrolytic extraction.

In the present state of the art, ferrochrome of low carbon content may be obtained by different means, depending on the carbon content it is desired to attain. Thus for carbon contents of about 1%, it is possible to start from carburized ferrochrome (with 6 or 10% carbon), part of the carbon thereof being oxidised either by blowing air into the liquid metal or by the reaction of the latter with a slag rich in Cr_2O_3. When it is desired to achieve lower carbon contents (of about 0.1%), it is necessary to make use of more complicated and more costly methods. Among them will be found in particular the Swedish cyclical process which comprises first the preparation of a carburized ferrochrome, followed by the elimination of the carbon therefrom by saturating the metal with silicon and, lastly, to make this metal react with a slag rich in Cr_2O_3. In a similar manner, the Ugine-Perrin process comprises the direct preparation of a ferrosilicon chromium and to make the latter react in two stages with a slag rich in Cr_2O_3. It is also possible to employ the Thermit reaction of the ore or of the pure chromium oxide, which yields a metal of very low carbon content, but generally contaminated by aluminium (up to 0.5% and more).

Recently methods have also been developed which make use of metallurgy under vacuum (Simplex process). They comprise in principle the reacting under vacuum of a ferrochrome of fairly high carbon content with a chromium ore or with a ferrochrome reoxidised in part. These

reactions are carried out in tunnel furnaces and yield in the first case a ferrochrome of very low carbon content but contaminated by the ore gang and by silicon, whereas in the second case the metal is much purer, but the cost of the process is very high.

It has also been tried to produce chromium by means of electrolysis. In aqueous solutions several industrial scale methods exist, which generally yield an impure metal (1% oxygen and much dissolved hydrogen) with poor current efficiencies. As regards the use of melted halides as electrolyte, the literature lists many laboratory studies, among which may be cited those of Krupp (1893), Nees (1942), Kroll, Hergert and Carmody (1950, Weill (1954), Andieux and Marion (1956). All these investigations are characterized by the fact that they make use of a chromium halide dissolved in a mixture of alkaline or alkaline-earths halides. As the electrolysis is carried out below the chromium fusion point the chromium is obtained in the shape of dendrites or of a powder, which must be separated from the alkaline salts by means of a suitable washing technology. Lastly the U.S. Pat. 2,398,591 in the name of A. Mitchell describes a method of production of chromium by the electrolysis of mixtures of fluorides containing chromium oxide (Cr_2O_3) and cryolite. In that case the electrolysis is carried out below the chromium fusion point, so that the difficulties of recovering the metal deposited on the cathode mentioned hereinbefore are again present.

In the field of electrolysis of melted oxides, O. A. Esin, in the work "Contemporary Problems of Metallurgy" (Publisher A. M. Samarin, translated from Russian, Consultants Bureau, New York, 1960, p. 374), mentions laboratory tests, in the course of which a refining—and not an extraction—electrolysis made it possible to obtain a deposit of chromium dissolved in melted copper providing the cathode, the anode being made of chromium. In that case, the electrolyte comprises a mixture of oxides containing boron oxide.

Also, M. Dodero and R. Mayoud describe in "Comptes Rendus de l'Académie des Sciences," vol. 242 (1956), pp. 124–126, laboratory tests in the course of which they were able to achieve a moderate chromium enrichment of a liquid iron on the arc electrolysis of a slag containing chromium oxide Cr_2O_3 dissolved in sodium silicate.

Whatever may be the case, it will be noted that present methods of production of ferrochrome or of chromium of low carbon content are generally complicated processes involving either costly installations comprising several furnaces, or costly reducing agents, such as aluminium, or yield a metal contaminated by oxygen and even by hydrogen.

Similarly, the attempts to develop methods of production making use of melted halides present many disadvantages, particularly when the metal is deposited in the solid state. It could of course be imagined to subject to electrolysis chromium oxide dissolved in a mixture of fluorides selected in such a manner that it is possible to obtain the chromium at the cathode in the liquid condition. However, the temperatures to be reached are so high that the losses of halides by volatilization would be prohibitive, calling for a very costly gas purification plant in order to prevent the contamination of the surrounding countryside. The same would be the case if it were enough to seek production of a chromium alloy, such as ferrochrome, by such process.

In this connection, the impurities, which might possibly be present, would produce emission of corrosive vapors. On occasion, should the charge of the furnace be damp, there might even be formation of gaseous hydrofluoric acid in the furnace, with all the serious consequences resulting therefrom. Similarly, the problem of the refractory material to be used as a crucible is substantially unsoluble from an economic point of view, carbon having to be ruled out, as it would carburize the chromium produced.

The aim of the present invention is to overcome the disadvantages of the said methods and to provide a process for the production of metallic chromium by means of fused electrolysis, on an industrial scale, starting with electrolyte of well specified composition so as to produce an industrially pure chromium at a very interesting cost price.

For that purpose, the process according to the invention includes the use of an electrolytic bath deriving from a ternary system selected among the group comprising the systems Cr_2O_3—CaO—Al_2O_3, Cr_2O_3—MgO—Al_2O_3, Cr_2O_3—CaO—MgO, Cr_2O_3—SiO_2—CaO and

Cr_2O_3—MgO—SiO

as well as the complex systems derived from compounds of the said ternary systems.

Indeed, it has been noted that, in a rather unexpected manner, it is possible to produce easily and economically chromium by means of an electrolytic bath with a composition in accordance with the specification given above. For instance, it is possible to find in the

CaO—MgO—Al_2O_3

system, a solvent of chromium oxide Cr_2O_3, which is selected so that the solution may contain more than 30% of Cr_2O_3, without the fusion point exceeding 1600° C. In any case, and although the theoretical temperature of inversion of the deoxidation reaction of Cr_2O_3 by the anodic carbon with formation of CO is about 1250° C., experience shows, in a rather unexpected manner, that even at 2000° C., and more, the kinetics of this thermal reduction is far lower than that of the electro-chemical reduction. It follows therefrom that the electrolysis may very well take place for example at 1850 or at 1900° C. without there being an exaggerated contamination of the chromium deposited on the cathode by the carbon. The range of composition for the electrolyte under consideration is therefore very large.

In order to limit the silicon content in the chromium deposited on the cathode while exhausting sufficiently the electrolytic bath of chromium, according to an advantageous form of embodiment of the object of the invention, the process comprises maintaining the quantity of silica in the electrolytic bath at a value below 50% by weight of the electrolyte.

According to a particularly advantageous form of embodiment of the object of the invention, the process comprises adjusting the total of the quantity of lime and magnesia with reference to the total of the quantity of silica and alumina in the electrolytic bath in a ratio by weight which shall not be less than .75.

The process according to the invention may also be advantageously used to prepare a chromium based alloy.

For that purpose, at least one or more metals having an affinity for oxygen less than, equal to, or slightly in excess of that of chromium are introduced in the electrolytic bath so that said metal or metals are deposited at the cathode alongside with the chromium and form an alloy with the latter. In the case where the affinity of the said metal or metals for oxygen is superior to that of chromium, it will be sufficient to maintain a cathodic current density sufficiently high or to exhaust the bath partially of chromium in order to achieve this. Or again, if the fusion point of the added metal is lower than the temperature of the electrolyte and of the melted cathodic metal, it is possible to introduce it directly in metal form in the electrolysis cell.

The invention also relates to an electrolysis cell to be used for working the said process.

Said cell comprises a container above which is mounted at least one carbon anode and the bottom thereof is provided with a cavity wherein terminates one lead of cathodic current, said cavity being intended to contain the metal, such as chromium, to be extracted, providing the cathode, an electrolyte being located above the latter and comprising said metal in the shape of an oxide compound, characterized in that the lead of cathodic current is effected by means of a cooled conductor so as to coat it with a protective layer of said solidified metal, a layer of the said liquid metal floating on top of the solidified metal.

Other details and features of the invention will become apparent from the description of the accompanying drawings, given hereinafter by way of non-limitative example, of several forms of embodiment of the process according to the invention and of cells which may, in particular, be used for working the said process.

FIG. 1 is an elevational view, partially broken away, of a first form of embodiment of the object of the invention.

FIG. 2 is an elevational view, partially broken away, of a second form of embodiment of the object of the invention.

In the two figures, the same reference numerals designate similar elements.

The electrolysis shown in FIG. 1 was used to carry out large scale laboratory tests.

It comprises in succession an outer casing **1** made from ordinary steel sheet, surrounded by a cooling pipe **2**, a watercooled hollow bottom **3**, a carbon free magnesia concrete inside lining **4**, a cathodic current lead comprising a copper tube **5** internally cooled by a circulation of water supplied through a pipe **6** and carried away through a pipe **7**, a steel component **8** screwed in the top end of the tube **5**, a chromium layer **9** providing the cathode, a graphite anode **10**, an electrolyte **11**, wherein dips the anode **10**, floating on the chromium layer **9**, a thermal screen **12** of heat-resisting steel, wherein are provided openings **13** permitting the progressive charging of the cell, three angles **14** mounted radially and carrying, on the one hand, the screen **12** and, on the other hand, a tubular sleeve **15** guiding the anode **10** and lastly removable steel lids **16** protected on their bottom faces by a layer of asbestos. The lids **16** are partially supported by the angles **14** and are used to maintain a reducing atmosphere in the cell in order to prevent the surface oxidization of the electrolyte **11**.

On account of the cooling of tube **5**, the component **8** is covered with a solidified protective layer **17** of chromium, the remainder of the layer **9** being in the liquid condition. When the cell is in normal operation, it is possible to maintain a layer of solid electrolyte **18** in contacting relationship with the lining **4**. It is, however, sufficient to increase the power slightly in order to melt the electrolyte charge completely. Lastly, the cell is carried on a tripod **19**, a tap hole **20** is provided for removing the metal **9** and another hole **21**, provided above the first tap hole **20** is provided to remove exhausted electrolyte.

The electrolysis cell shown in FIG. 2 may be used on an industrial scale. It comprises substantially an outer casing **1** made from ordinary steel sheet cooled, if need be, by a water circulation not shown, walls **22** and a bottom **23** made from refractory bricks, a carbon free magnesia concrete inside lining **4**, cathodic current leads comprising copper tubes **5** on the top of each of which is provided a mild or stainless steel component **8** and cooled internally by a water circulation, a layer of chromium **9** providing the cathode, a plurality of anodes **10** made from, for example Söderberg quality, carbon, an electrolyte **11** provided on top of the chromium layer **9**, a vault **16** made from silica provided with bores **25** connected to pipes, not shown in the figure, for exhausting the gases released at the anode **10**, bores **25** connected to feed hoppers, also not shown in the FIG. 2, and lastly sight bores **26**.

When the cell is in normal operation, it may be of advantage to protect the lining **4** by a layer of solid electrolyte **18**.

Lastly, a tap hole **20** enables the removal of the metal built up on the cathode while another hole **21** is used to remove exhausted electrolyte. Where the anodes **10** pass through the vault **16**, the leak tightness is provided by means of an appropriate device **27**. The vault **16** maintains a reducing atmosphere inside the furnace in order to prevent the surface oxidization of the electrolyte. However, in certain cases where a slight surface oxidization of the bath is permissible, said vault need not be provided.

FIRST TEST

The cell used for this test is shown in FIG. 1.

4 kgs. of twice refined ferrochrome were tipped, prior to electrolysis, on the hearth of the cell, the said ferrochrome containing 73.20% of chromium, 0.45% of silicon and 0.081% of carbon. The anode **10** being provided at a certain distance above the ferrochrome, an arc was then established between the said anode **10** and the ferrochrome. Subsequently a charge, comprising 20 kgs. of a mixture of ferrochromite based ore, was immediately, but gradually introduced in the cell. This mixture was adjusted so as to obtain a gang comprising 43.5% of lime, 10% of magnesia, 23.25% of alumina and 23.25% of silica, which corresponds to a ratio by weight:

$$\frac{CaO+MgO}{SiO_2+Al_2O_3}$$

of 1.15.

Also, its Cr_2O_3 content was assumed equal to 5%.

As soon as the charge had melted, a temperature comprised between 1,750° C. and 1,850° C., measured by means of a vanishing filament optical pyrometer was maintained in the electrolyte **11**.

The current intensity mounted to 1,050 amps for a terminal voltage of 25 v., while, the anode **10** dipping in the electrolyte **11**, the distance between such anode and the chromium layer **9** providing the cathode exceeded 5 cm., these conditions being maintained for five hours.

During the electrolysis, regular additions of ferrochromite were carried out, in order to maintain the average concentration of the bath in Cr_2O_3 around 15%.

It was necessary to maintain the anode effect for the whole duration of the test, in order that the available power should be sufficient for working at constant temperature.

Under normal conditions of electrolysis, the tension at the cell terminals was less than 10 v. for 1,050 amps.

After five hours, the anode was withdrawn from the electrolyte **11** and the cell was left to cool slowly. When the cell had reached substantially ambient temperature, the exhausted electrolyte and the metal produced were withdrawn. The electrolyte still contained about 4% of Cr_2O_3, while the collected metal met the following analysis.

	Percent
Cr	74.4
Si	0.42
Al	0.06
C	0.025

The remainder comprised substantially iron.

The cathodic current efficiency was about 60%, which may be considered as very satisfactory, considering the fairly small scale at which the test was carried out. The current intensity used for this test corresponded to an average current density of about 350 amps/dm.^{2}.

SECOND TEST

The cell used for this test is shown in FIG. 1.

4 kgs. of chromium metal were laid, prior to electrolysis, on the hearth of the cell, the refractory lining of which was made up from electrically melted magnesia. The analysis of the chromium brought in was as follows.

	Percent
Cr	99.3
Al	0.15
Si	0.07
C	0.03
Fe	0.4

An arc was then established between the anode **10** and the chromium. Subsequently a charge comprising 20 kgs. of a mixture of ore based on pure chromium oxide was immediately, but gradually introduced in the cell. This mixture was made up so as to achieve a synthetic gang comprising 46% of lime, 6.3% of magnesia and 47.7% of alumina which corresponds to a ratio by weight:

$$\frac{CaO+MgO}{SiO_2+Al_2O_3}$$

of 1.095. Also, its Cr_2O_3 content was assumed equal to 5%.

As soon as the charge had melted, a temperature comprised between 2000° C. and 2100° C. measured by means of a vanishing filament optical pyrometer was maintained in the electrolyte **11**. The average current intensity amounted to 1,150 amps for a terminal voltage of 26 v., while the distance between the anode **10** and the cathode **9** exceeded 5 cm., these conditions being maintained for about 5 hours. During the electrolysis regular additions of chromium oxide were carried out in order to maintain the average concentration of the bath in Cr_2O_3 around 15%. It was necessary to maintain the anode effect for the whole duration of the test, in order that the available power should be sufficient for working at constant temperature. Under normal conditions of electrolysis, the tension at the cell terminals was less than 10 v. for 1.050 amps. After five hours, the anode was withdrawn from the electrolyte **11** and the cell was left to cool slowly down to substantially ambient temperature. At that moment, the exhausted electrolyte and the metal produced were withdrawn. The electrolyte still contained about 6% of Cr_2O_3, the collected metal meeting the following analysis.

	Percent
Cr	99.1
Si	0.02
Al	0.08
C	0.007

The remainder comprised mainly iron which could originate from pieces of oxide fallen from the thermal screen in heat-resisting steel.

The cathode current efficiency was about 50%, which may be considered a success, considering the scale at which the test was carried out. The current intensity used for this test corresponded to an average current density of about 600 amps/dm.^{2}.

It should be noted, as follows moreover from what has been stated hereinbefore, that the cathodic liquid chromium is carried on a solid layer formed by one or more refractory oxides which do not react with the chromium. The electric cathodic contact between the liquid chromium and the feed of cathodic current is effected by means of a conductor cooled so as to become coated with a layer of solidified chromium. This has for its aim to prevent any contamination of the chromium produced at the cathode by the metal or metals comprising the cathodic current feed. Although this is not absolutely essential, it may be of a practical interest for the electrolysis cell to be built with dimensions such that the liquid electrolyte is never in immediate contacting relationship with the refractory walls and bottom but rather with a crust of solidified electrolyte. This precaution may indeed lead to a fairly important economy of refractory materials.

As follows from the said tests, the electrolyte may comprise three or a plurality of the following compounds: Cr_2O_3, CaO, SiO_2, Al_2O_3 and MgO. Thus in particular a mixture of oxides comprising 46% of CaO, 6.3% of MgO and 47.7% of Al_2O_3 by weight may dissolve up to 30% of Cr_2O_3 by weight while maintaining all the time a melting temperature below 1600° C. Mixtures of this kind, when subjected to electrolysis, have revealed themselves extremely interesting. Indeed, for anodic and cathodic current densities close to 250 amps/dm.^{2} and for distances between anode and cathode of not less than 5 cms., it is possible to maintain voltages at the cell terminals within the limits of 8 and 10 v., the temperature of the electrolyte not exceeding 1700° C. The presence of moderate quantities of silica, such that the index of basility;

$$\frac{CaO+MgO}{SiO_2+Al_2O_3}$$

shall be maintained equal to or higher than unity, improves still further the properties of such electrolytes, while maintaining a silicon content of less than 1 or 2% in the cathodic metal for residual Cr_2O_3 contents in the electrolyte of less than 5%.

Of course, other oxides may still be present in the electrolyte as is the case, for example, when ores such as ferrochromite are used as electrolyte. It is then sufficient to adjust the composition of the gang in such a manner that it corresponds approximately to a mixture of oxides considered as particularly interesting as a solvent of Cr_2O_3.

The anode used in the electrolysis cell for working the process according to the invention may be of amorphous carbon, of graphite or more currently of Söderberg type.

The tapping of the metal deposited on the cathode, on the one hand, and of the exhausted electrolyte on the other hand, does not raise any special problems and is of current metallurgical practice.

The metal produced by electrolysis is essentially characterized by a very low carbon content (less than 1%) and a low silicon content (generally less than 2%). The content of other impurities is conditioned by the purity of the electrolyte. Thus all of the iron contained in the electrolyte passes into the chromium deposited at the cathode. The same would be the case for any other element having an affinity for oxygen lower than, equal to or slightly in excess of that of chromium, i.e. for example, manganese, cobalt, copper, nickel, silicon and aluminium. The silicon content of the metal produced at the cathode is essentially conditioned by the index of basicity of the electrolyte, by its silica content and by its degree of final exhaustion. If said index is maintained at a value equal to or higher than unity, that the silica content is less than 25% and the electrolysis is stopped at the time when about 5% Cr_2O_3 remain in the electrolyte, it is possible to achieve silicon contents of less than 1%. Under those conditions, and insofar as the electrolyte does not contain inpurities more reductible than Cr_2O_3, it is possible to produce a chromium of about 99% or more.

On the other hand, if a chromium with a higher silicon content is desired, it will be sufficient to maintain the index of basicity of the electrolyte sufficiently low, for example below .75 and/or a silica content exceeding 25% and to continue the electrolysis until a high rate of exhaustion of the electrolyte is reached.

In the case when a chromium ore or a mixture of ores thereof is used to make up the electrolyte, there should be added to said ore or mixture of ores the oxides needed in order that the overall composition of the electrolyte shall approximate the ideal compositions hereinbefore mentioned.

If the chromium ore mixture contains iron, it is possible to produce by electrolysis a chromium with a low iron content by carrying out beforehand an operation to remove the iron.

According to the invention, the ore is then subjected to an electrolysis similar to that permitting to achieve a chromium with little impurities, without, however, proceeding as far as to exhaust the chromium from the electrolyte. It is thus possible to produce, on the one hand, an electrolyte containing 20% or more of Cr_2O_3, for example, but the iron of which has been removed, which is afterwards subjected to an exhaustion electrolysis in another electrolysis cell of the type hereinbefore described and, on the other hand, a ferrochrome of low carbon and silicon content, having a high commercial value compared with heavily carburized chromium pig iron produced by a conventional iron removal method, such as a reducing melt in an electric furnace.

It must be well understood that the invention is not limited to the forms of embodiment described, and that many changes may be contemplated without departing from the scope of the present patent application.

Thus the electrolyte could contain minute additions of other oxides or salts than those comprised in the ternary systems hereinbefore cited such as BaO, B_2O_3, NaF, CaF_2 and having for their object to reduce the melting temperature thereof or to increase the electric conductivity thereof.

I claim:

1. A process for the production of chromium of low carbon content by means of fused electrolytic extraction including the use of an electrolytic bath deriving from a ternary system selected among the group comprising the systems Cr_2O_3—CaO—Al_2O_3, Cr_2O_3—MgO—Al_2O_3,

Cr_2O_3—CaO—MgO, Cr_2O_3—SiO_2—CaO

and Cr_2O_3—MgO—SiO as well as the complex systems derived from compounds of the said ternary systems.

2. A process as claimed in claim **1** comprising using a cathode formed by the metal to be extracted, such as chromium or a chromium alloy with another metal present in the electrolyte in the form of oxide.

3. A process as claimed in claim **1**, which comprises maintaining in the electrolytic bath the silica content below 50% by weight of the electrolyte.

4. A process as claimed in claim **1**, which comprises adjusting the total of the quantity of lime and magnesia with reference to the total of the quantity of silica and alumina in the electrolytic bath in a ratio by weight which shall not be less than .75.

5. A process as claimed in claim **4** wherein the said ratio by weight is not less than 0.9.

6. A process as claimed in claim **1**, which comprises plunging the anode in the electrolytic bath and adjusting the criteria of the electrolysis, such as the current intensity and the tension at the electrodes of the cell in which the electrolysis takes place, in such a manner as to achieve a condition free from anode effect in the bath.

7. A process as claimed in claim **1**, which comprises adjusting the criteria of the electrolysis in such a manner as to achieve a condition with anode effect in the bath.

8. A process as claimed in claim **1**, which comprises placing the anode a certain distance above the surface of the electrolytic bath and adjusting the criteria of the electrolysis so as to establish an arc between the anode and the surface of the said bath, so as to provide an arc system.

9. A process as claimed in claim **1**, wherein the electrolyte is subjected to a preliminary electrolysis in order to remove from the bath the metals which are more easily reductible than the chromium such as iron for example, to remove also the alloy, such as ferrochrome, deposited on the cathode, as well as to subject the electrolyte purified in this manner to a second electrolysis so as to produce the chromium.

10. A process as claimed in claim **1**, wherein one or more metals having an affinity for oxygen less than, equal to, or slightly in excess of that of chromium are introduced in the electrolytic bath so that said metal or metals are deposited at the cathode alongside with the chromium and provide an alloy with the latter.

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U.S. Cl. X.R.

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