(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 219 157 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **86201679.7**

(51) Int. Cl.⁴: **C25C 3/28** , C25C 3/00

(22) Date of filing: **29.09.86**

(30) Priority: **02.10.85 NL 8502687**

(43) Date of publication of application:
22.04.87 Bulletin 87/17

(84) Designated Contracting States:
BE DE FR GB IT NL SE

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(54) Process for the electrolytic production of metals.

(57) A process for the production of metals Me by electrolysis in the presence of a salt melt (8) of one or more alkali metal or alkaline earth metal halides which comprises introducing a metal halide MeX_n - (5) into a cathode (3) consisting of a molten metal M or a molten alloy $M.Me_x$, in which Me represents a metal selected from Ti, Ta, Al, Zr, W, Nb, V, Mo, In, Ag and Sb, M represents a metal selected from Zn, Cd, Sn, Pb, In, Bi and Ga, X represents halogen and n represents the valency of the metal Me, thus producing an alloy $M.Me_y$, y:x being > 1, withdrawing alloy $M.Me_y$ from the cathode and recovering metal Me from the alloy.

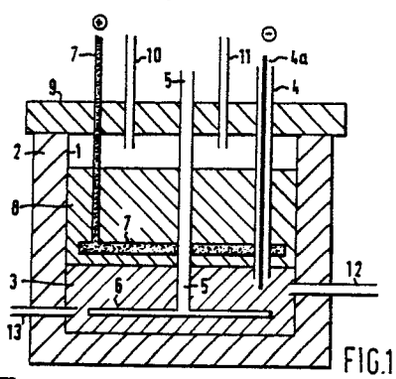

FIG.1

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PROCESS FOR THE ELECTROLYTIC PRODUCTION OF METALS

The invention relates to a process for the electrolytic production of metals from metal halides in the presence of a salt melt of one or more alkali metal or alkaline earth metal halides, in particular chlorides, an example thereof being production of titanium from titanium tetrachloride.

Winning metals by electrolysis in the presence of molten salts is an area in which increasing research is being carried out. An embodiment of this process is known from US-A-2757135. In this event titanium tetrachloride is supplied to the electrolysis cell by introducing into the salt melt. In practice, that process has to be carried out with a diaphragm that prevents the flow of titanium in lower valencies to the anode. If this were not done, the titanium would be re-oxidized at the anode to tetravalent titanium and would thus give rise to a loss of current and raw material. Furthermore, the build-up of titanium in the diaphragm shortens its life, which is a significant disadvantage.

The present invention proposes a process for the production of metals Me by electrolysis in the presence of a salt melt of one or more alkali metal or alkaline earth metal halides which comprises introducing a metal halide MeX_n into a cathode consisting of a molten metal M or a molten alloy $M.Me_x$, in which Me represents a metal selected from Ti, Hf, Ta, Al, Zr, W, Nb, V, Mo, In, and Ag, M represents a metal selected from Zn, Cd, Sn, Pb, In, Bi and Ga, X represents halogen and n represents the valency of the metal Me, thus producing an alloy $M.Me_y$, y:x being > 1, withdrawing alloy $M.Me_y$ from the cathode and recovering metal Me from the alloy.

The invention will be discussed in more detail with reference to figures 1 and 2, which illustrate possible electrolytic cells, taking the electrolysis of titanium tetrachloride to produce metallic titanium in a liquid zinc cathode as example.

In Fig. 1 cell 1 is in a jacket of thermally insulating material 2, for example refractory brick. Cathode 3 consists of liquid zinc to which current is fed via insulating pipe 4 and feed rod 4a. Supply of titanium tetrachloride takes place via pipe 5 and distributor 6, for example a metal grid with outlets at intervals or a body of porous ceramic material. Anode 7 is positioned in electrolyte 8 near the interface between cathode and electrolyte. The horizontal surface area of the anode is chosen to be as large as possible. Electrolyte 8, for example a lithium chloride/potassium chloride melt, is heated to a high temperature, for example 350 to 900 °C or higher if operations are carried out under pressure. Through lid 9 runs a supply pipe 10 for inert gas, for example argon, and a discharge pipe 11 for chlorine gas which is generated at the anode. The current and the supply of titanium tetrachloride are adjusted to match each other such that all or substantially all titanium is reduced in the cathode, thus forming a zinc/titanium alloy. This means that the anode does not need to be shielded by a diaphragm. This can be achieved with, for example a current of at least 4 Faraday per mol titanium tetrachloride. Vaporization of titanium tetrachloride before its introduction into the cathode is not necessary, since its temperature rises in any case to above its boiling point (136 °C) during its passage through the salt melt. If desired, the cell can also be provided with means for a correct temperature control of the process. The space above electrolyte 8 can also be cooled or any vaporized salt melt of zinc can be internally or externally condensed and fed back. Supply and discharge of cathode liquid takes place via lines 12 and 13, in particular in the continuous embodiment. The titanium content in the Zn/Ti alloy will be allowed to increase to a predetermined value, preferably between 6 and 20 %wt. Recovery of titanium metal from the alloy may be carried out by conventional methods, e.g. by distilling off cathode metal.

Figure 2 shows a cell with a vertically positioned anode. The same reference numerals have been retained for the same elements of the construction. In the salt melt a tray 14 is placed in which liquid zinc is present. Titanium tetrachloride vapour now enters via perforations in the lower part of supply pipe 5. Anode 7 is constructed as a closed cylinder which completely surrounds the cathode.

Although in the preceding section the process of this invention has been described by reference to the most preferred embodiment, i.e. production of titanium from titanium tetrachloride employing a liquid zinc cathode, the invention is not limited thereto. Analogous processing can be carried out with different cathode materials, i.e. cadmium, tin, lead, bismuth, indium and gallium, from which tin and lead are preferred. Likewise other feedstocks may be processed, i.e. halides of tantalum, aluminium, zirconium, tungsten, nyobium, vanadium, molybdenum, indium, silver and antimony. Preferred metal halides to be processed are those of tantalum, tungsten, vanadium and nyobium. The preferred halogen atom is chlorine, as it is for the molten salt compositions.

It is not known to what extent the production of metal Me proceeds via the direct electrolytic conversion of for example $Ti^{4+} \rightarrow + 4e \rightarrow Ti$. Introduction of $TiCl_4$ into a liquid zinc cathode at elevated

temperature may result in a chemical reduction of metal Me to lower valencies, for example $2TiCl_4 + Zn \rightarrow 2TiCl_3 + ZnCl_2$, this may then be followed by electrolytic reduction of trivalent titanium to metallic (zerovalent) titanium, coupled with electrolytic regeneration of cathode material by reducing divalent zinc to metallic (zerovalent) zinc. Such combined chemical and electrolytic reductions of metal Me in a higher valency to zerovalent metal are included expressis verbis in the scope of this invention, so is the production of zerovalent antimony from $TaCl_5$ in a liquid zinc cathode which probably proceeds entirely via chemical reduction by metallic zinc and electrolytic regeneration (reduction) of cathode material. What is essential to this invention is the application of an electrolytic cell with a liquid metal or alloy cathode, an introduction of metal halide MeX_ndirectly into the liquid cathode and production of (zerovalent) metal Me within the cathode material, the latter as distinguished from production of metal Me somewhere else, i.e. in the molten salt electrolyte or by deposition on a second or auxiliary cathode. Absence of a diaphragm is also important.

The salt melts may be free from impurities but this is not strictly necessary, while in addition it may be advantageous to work under an inert atmosphere of, for example, argon or nitrogen. Examples of suitable salt melts are LiCl/NaCl, NaCl/KCl, LiCl/KCl, $LiCl/CaCl_2$, $NaCl/BaCl_2$ and $KCl/CaCl_2$, but, as has already been pointed out, the invention is not limited to the above-mentioned melts.

In principle, suitable processing temperatures are above the melting point of the cathode material and below the temperature at which that material has such a vapour pressure that undesirably large losses occur. Preferred temperatures are between 400 and 900 °C, for zinc 425 to 890 °C, for cadmium 400 to 700 °C. Similarly, the processing temperature should not be so high that loss of molten salt electrolyte by evaporation or decomposition becomes substantial.

The current and the supply of metal halide feedstock are so adjusted that complete reduction of metal Me in the cathode can take place. Preferably, at least n $F.mol^{-1}$ metal halide MeX_n is supplied, n being the valency of the metal. The current is, however, restricted to a certain maximum, since deposition of salt-melt metal in the cathode should preferably be prevented as far as possible. The feedstock should preferably be introduced under homogeneous distribution into the cathode. The easiest way for achieving this is by using feedstocks that are in gaseous form on the moment of their introduction into the cathode material. However, introduction into the cathode of compounds in finely dispersed, solid form is also included within the scope of this invention. This all results in no metal Me, or practically none, in any valency ending up in the salt melt. It is then not necessary to employ a diaphragm to shield the anode, so that no undesired current and voltage losses occur, resulting in great technical and economical benefits. Cells having no diaphragm are preferred.

In the alloy $M.Me_y$ that is withdrawn from the electrolysis cell y represents the atomic ratio of Me to M. This ratio will usually be kept below 0.5, preferably below 0.3. For easier ways of recovering metal Me from the alloy it is preferred to process alloys in which the content of metal Me is of from 6 to 20 %wt, based on the weight of the alloy.

The invention is elucidated below by a number of experiments.

Example I

a. 1.5 kg of eutectic LiCl/KCl mixture (59 : 41 mol) was purified by passing HCl gas through it at above its melting point for 8 hours. The HCl forces the equilibria a) and b) shown below to the left, so that an anhydrous, almost oxygen-free melt is obtained.

a) $Cl^- + H_2O \rightarrow HCl + OH^-$

b) $2CL^- + H_2O \rightarrow 2HCl + O^{2-}$

Residual oxygen compounds and metallic impurities are then removed by electrolysis under vacuum at a cell voltage of 2.7 V.

An electrolytic cell of externally heated stainless steel was employed with a molten zinc cathode (90 g) which was placed in a holder of Al_2O_3 on the bottom of the cell. A graphite rod served as anode, no diaphragm was used and 250 g salt melt was used as electrolyte. The cell voltage was 5.0 V, the cathode potential was -2.0 V (relative to an Ag/AgCl reference electrode) and the other conditions are given in Table I. The $TiCl_4$ was injected as a liquid in an argon stream and fed into the cathode. An argon atmosphere was maintained above the salt melt. In all experiments a current of 6 $F.mol^{-1}$ $TiCl_4$ was employed. The following results were determined by microprobe and chemical analysis of the cooled solids.

Table I

Temp (0 °C)	Time (hr)	$TiCl_4$ $ml.hr^{-1}$	Current density $(A.cm^{-2})$	Cathode (% g/g) Zn	Ti	Li	K	Melt (% g/g) Ti	Zn
500	2.5	6.0	0.18	97.1	0.22	0.18	0.12	< 0.001	< 0.003
700	7.5	0.6	0.18	95.7	2.73	0.38	0.09	< 0.02	0.02
700	5	2.0	0.60	91.6	3.41	0.39	0.13	< 0.001	< 0.0005
450	1.0	1.25	0.38	99.4	0.14	0.24	0.06	< 0.002	0.02

b. Alloy produced in the first experiment of Table I was subjected to distillation in order to remove all zinc. Upon analysis the remaining residue appeared to consist of very pure titanium.

Example II

Employing various cathode materials $TiCl_4$ was electrolysed in the manner described in example Ia, under the same conditions except those indicated in Table II.

Table II

Temp (0 °C)	Time (hr)	$TiCl_4$ (ml)	$TiCl_4$ (ml.hr^{-1})	Current density (A.cm^{-2})	Cathode M	Cathode (% g/g) M	Cathode (% g/g) Ti	Cathode (% g/g) Li	Cathode (% g/g) K	Melt (% g/g) M	Melt (% g/g) Ti
825	4.5	25	1.7-10.3	0.5-3.0	Zn	89	8.3	-	0.04	0.02	0.01
650	5.5	20	1.7-6.5	0.5-2.0	Cd	87	3.8	1.6	0.8	< 0.02	< 0.01
800	5.5	19	1.7-6.5	0.5-2.0	Sn	81	8.3	2.3	0.04	< 0.1	< 0.1
800	6.0	20	3.4	1.0	Pb	84	5.1	0.2	-	< 0.03	< 0.003
800	6.0	23	1.7-6.9	0.5-2.0	Bi	95	3.9	0.3	0.2	0.09	< 0.003
800	4.8	17	3.5	1.0	In	94	3.6	1.5	0.12	0.03	0.004
825*	3.8	15	1.7-8.5	0.5-2.5	Zn	94	2.2	-	< 0.001	0.15	0.06
800*	3.8	13	3.4	1.0	Sn	74	8.0	-	0.3	0.05	0.017

* molten salt electrolyte NaCl/KCl.

Example III

Employing various metal halide feedstocks and various cathode materials, experiments were run as described in example I under the same conditions except as those indicated in Table III.

Table III

Cathode M	Feedstock MeX_n	Temp. (° C)	Time (min)	Feedrate ($g.hr^{-1}$)	Current ($F.mol^{-1}$)	Current density ($A.cm^{-2}$)	Cathode analysis (% g/g) M	Me	Li	K	Electrolyte analysis (% g/g) M	Me
Zn	$TaCl_5$	480	34	8.9	7.5	1	98.7	0.32	1.22	0.27	< 0.002	< 0.02
Zn	$AlCl_3$	695	300	5.5	4.5	1	93	4.40	5.7	0.17	0.059	< 0.01
Al	$AlCl_3$	720	360	5.9	4.2	1	*					
Zn	$ZrCl_4$	745	140	6.5	7.2	1	86	1.8	1.6	< 0.1	0.061	< 0.2
Zn	WCl_6	735	90	< 2	> 9.0	1	86.4	0.48	2.66	0.004	0.17	< 0.05
Sn	$NbCl_5$	735	120	1.5	> 7.5	0.5	92	0.044	3.3	< 0.05	0.024	0.01
Ga	VCl_3	800	30	2.4	> 4.5	0.5	88.3	0.14	< 0.001	< 0.003	0.003	0.001
Ga	$MoCl_5$	800	30	1.8	>7.5	0.5	88.4	1.1	0.17	0.06	0.10	0.005
Zn	AgCl	735	130	6.0	4.4	1	98.2	0.41	0.94	0.10	0.52	0.04
Zn	$InCl_3$	765	240	6.0	5.1	0.5	89.0	10.2	0.84	< 0.10	0.01	0.15

Electrolyte: LiCl/KCl

* = 45% weight increase of Al.

Claims

1. A process for the production of metals Me by electrolysis in the presence of a salt melt of one or more alkali metal or alkaline earth metal halides which comprises introducing a metal halide MeX_n into a cathode consisting of a molten metal M or a molten alloy $M.Me_x$, in which Me represents a metal selected from Ti, Hf, Ta, Al, Zr, W, Nb, V, Mo, In, and Ag, M represents a metal selected from Zn, Cd, Sn, Pb, In, Bi and Ga, X represents halogen and n represents the valency of the metal Me, thus producing an alloy $M.Me_y$, y:x being > 1, withdrawing alloy $M.Me_y$ from the cathode and recovering metal Me from the alloy.

2. A process as claimed in claim 1, in which metal halide MeX_n is distributed in gaseous form through the liquid cathode material.

3. A process as claimed in claim 1 or 2, in which X represents chlorine.

4. A process as claimed in any one of claims 1 to 3, in which the withdrawn alloy comprises 6 to 20 %wt of metal Me, calculated on the weight of the alloy, and in which Me is titanium.

5. A process as claimed in any one of claims 1 to 4, in which a current of at least n $F.mol^{-1}$ is employed, n being the valency of metal Me in the feedstock.

6. A process as claimed in any one of claims 1 to 5, in which the molten salts are chlorides.

7. A process as claimed in any one of claims 1 to 6, in which metal Me is selected from Ti, Ta, W, V and Nb.

8. A process as claimed in claim 7, in which metal Me is Ti.

9. A process as claimed in any one of claims 1 to 8, in which metal M is Zn, Sn or Pb.

10. A process as claimed in claim 9, in which metal M is Zn.

11. A process as claimed in any one of claims 1 to 10, which is carried out in an electrolytic cell having no diaphragm.

12. A process as claimed in claim 1 and substantially as hereinbefore described with particular reference to the Examples.

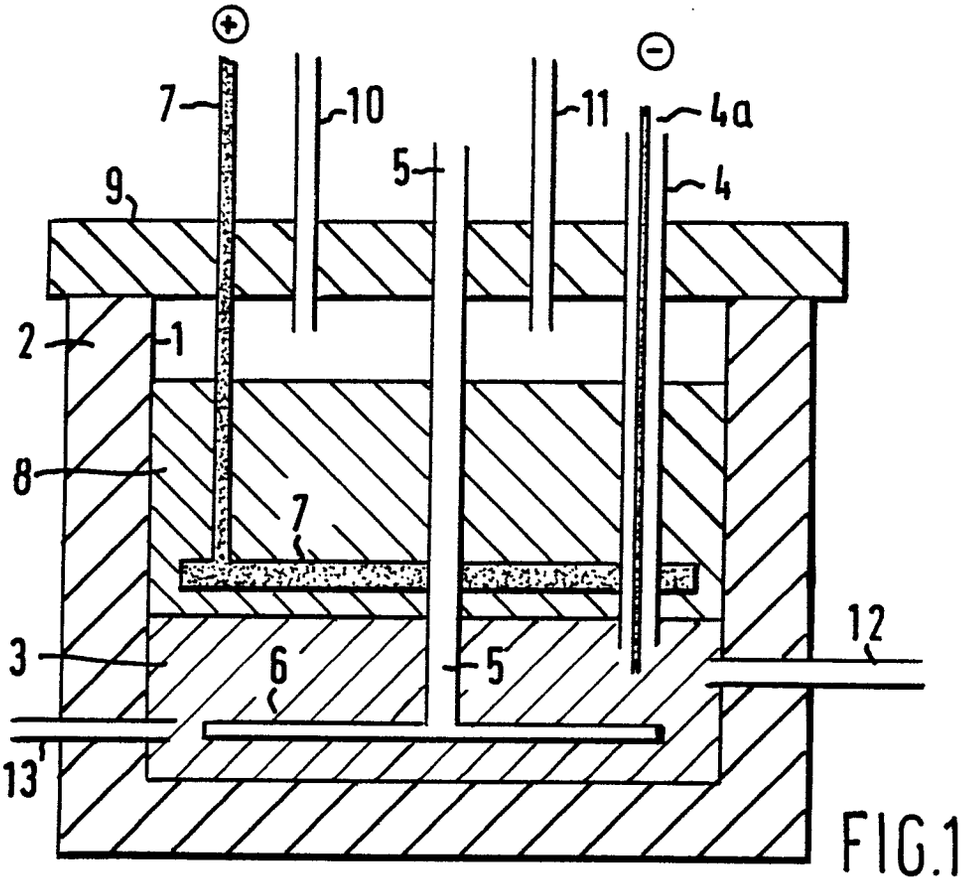

FIG.1

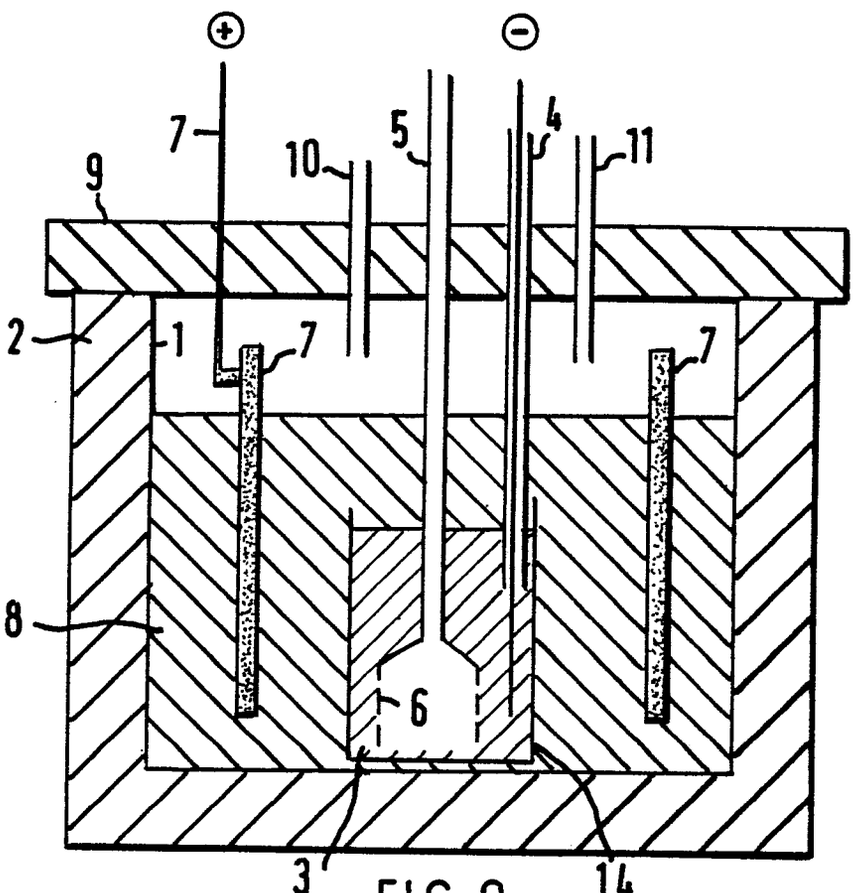

FIG.2

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 86 20 1679

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	EP-A-0 039 873 (METALS TECHNOLOGY & INSTRUMENTATION) * Page 9, lines 9-27; page 14, lines 17-30; pages 15, 16; claims ; figure 3 *	1,2,3, 6,7,8, 9,11, 12	C 25 C 3/28 C 25 C 3/00
X	DE-B-1 139 985 (TIMAX) * Column 7, lines 1-4; column 9, lines 30-44; columns 13,14; claims *	1,2,3, 6,7,8, 11	
A	GB-A- 660 908 (A. JOHNSON & CO.) * Page 2; claims *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 25 C 3

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	13-01-1987	GROSEILLER PH.A.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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