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(54) Title: PROCESS FOR SEPARATING HAFNIUM AND ZIRCONIUM

(57) Abstract: The invention is directed to a process for separating a mixture comprising hafnium and zirconium. The process of the present invention comprises a step in which a molten metal phase comprising zirconium and hafnium dissolved in a first metal M¹ and a second metal M² is contacted with a molten salt phase comprising at least one metal halide M³Z, wherein M³ is a metal that is less electropositive than zirconium and hafnium, and at least one salt of one or more metals M⁴, wherein M⁴ is a metal from Group 1 or Group 2 of the Periodic Table, whereby at least part of said hafnium is transported from said molten metal phase to said molten salt phase.



Title: Process for separating hafnium and zirconium

The invention is directed to a process for separating a mixture comprising hafnium and zirconium. Zirconium and its alloys have high melting points and a high corrosion resistance. Consequently, zirconium is applied in chemical industry and in particular in nuclear reactors. Zirconium has a very
5 low absorption coefficient for neutrons, which makes this metal pre-eminently suitable as construction material in nuclear reactors.

In nature zirconium is nearly always found in combination with hafnium. Contrary to zirconium, hafnium has a high absorption coefficient for neutrons, which makes this metal suitable as neutron absorber in nuclear
10 reactors. Chemically the metals zirconium and hafnium strongly resemble each other. In the application of the metal zirconium as construction material in nuclear reactors, in which the low absorption coefficient for neutrons is essential, the metal zirconium should have as low a content of hafnium as possible.

15 Conversely, traces of zirconium in hafnium hardly have any effect on the absorption coefficient for neutrons.

Zirconium has a favorable strength to weight balance. This favorable strength to weight balance is only attained if the percentage of oxygen in the metal zirconium or the related alloys dissolved in it is sufficiently low. If the
20 percentage of dissolved oxygen in the metals or in the alloys becomes too high, the material in general will become too brittle and therefore technically less usable.

US-A-4 072 506 describes a process for separating hafnium from zirconium from a mixture containing these metals. In this known process the
25 mixture is dissolved in a molten metal phase that comprises a single solvent metal. Although copper is listed as one of several suitable solvent metals among cadmium, lead, bismuth and tin, it is taught in US-A-4 072 506 that in practice the best metal for use as a solvent metal is zinc. The molten metal phase is contacted with a fused salt phase, whereby hafnium is transported

from the molten metal phase to the fused salt phase. The fused salt phase also contains a zirconium salt, which can be reduced to zirconium and transported to the molten metal phase. The process of US-A-4 072 506 further involves a distillation step in which zinc is distilled off from the metal phase which
5 comprises zirconium as its main constituent. The zinc is recycled and the zirconium is obtained as a product stream.

The present invention seeks to improve the process of US-A-4 072 506, in particular by providing a purification process that results in a much higher separation factor β , that can be carried out at lower
10 temperatures and that can be combined with electrolytic refining steps, either in the step of production of intermediate materials or in the step of recovery of the zirconium and/or hafnium, or both.

Thus in a first aspect, the present invention is directed to a purification process for separating a mixture comprising hafnium and
15 zirconium, comprising the steps of:

- providing a molten metal phase comprising a first metal M^1 and a second metal M^2 ;
- providing a molten salt phase comprising at least one metal halide M^3Z , wherein M^3 is a metal that is less electropositive than zirconium and
20 hafnium, and one or more salts of one or more metals M^4 , wherein M^4 is a metal from Group 1 or Group 2 of the Periodic Table;
- feeding said mixture comprising hafnium and zirconium to said molten metal phase; and
- contacting said molten metal phase and said molten salt phase,
25 whereby at least part of said hafnium is transported from said molten metal phase to said molten salt phase.

The metals M^1 and M^2 are preferably chosen such that they are more noble than Zr (and Hf). In principle all metals from Groups 5-15 and Periods 4-6 from the Periodic Table (all references to Groups and Periods in
30 the Periodic Table as used herein are according to the IUPAC definition) would

qualify, because they have an electropositivity that is lower than that of Zr, which corresponds to an *electronegativity* that is higher. The electronegativity of Zr is 1.33 Pauling units and that of Hf 1.3 Pauling units. Thus metals having an electronegativity of more than 1.33 would be suitable. In practice,
5 M¹ and M² are preferably each independently selected from Cu, Sn, Ag, Sb, Zn, Pb, Bi, Fe, Ni, Cd, Si and Co. It is preferred to select M² such that it lowers the melting point of M¹, which is favorable in terms of energy consumption of the process. Operating the process at lower temperatures also provides the advantage that refractory problems are reduced, while the lifetime of the
10 installation is increased and operational costs are reduced.

The molten salt phase comprises at least one metal halide M³Z, preferably a metal chloride M³Cl_x, where *x* represents an integer corresponding to the valence of M³. It is preferred that the metal halide corresponds to the metal in the molten metal phase, *viz.* M³ is the same as M¹
15 and/or M². More preferably a mixture of metal halides M³Z is used, wherein a portion of the total M³ present corresponds to M¹ and another portion equals M². In a highly preferred embodiment, the molten metal phase comprises Cu and Sn and the molten salt phase comprises CuCl₂ and SnCl₂.

The molten salt phase furthermore comprises at least one salt of one
20 or more metals M⁴, wherein M⁴ is a metal from Group 1 (alkali metals) of the Periodic Table, preferably Na or K; or Group 2 (alkaline earth metals) of the Periodic Table, preferably Mg or Ca. Addition of this salt lowers the melting point of the molten salt phase, which is favorable in terms of energy consumption of the process. It is preferred to use halides for this purpose, in
25 particular chlorides. M⁴ is preferably selected from Na, K, Ba, Sr and Ca. Preferably the salt or salts of M⁴ is a combination of a chloride or fluoride of Ca, Na and/or K. Most preferred is CaCl₂ which is optionally supplemented with NaCl and/or KCl. To obtain metallic zirconium that meets the requirements for nuclear application, liquid metal mixtures can be used that
30 are obtained in the manner described hereinbelow. First the separation

process as set out above will be explained in more detail below, with reference to the figures.

Figures 1-8 schematically show different embodiments of the present invention. These are in particular embodiments in which the preprocessing of the starting materials and the postprocessing of the products that are
5 respectively fed to and obtained from the purification step (2) described above are carried out in various manners.

Figure 1 schematically depicts a processing route for producing purified zirconium. In this embodiment a ZrO_2 feed contaminated with HfO_2 is introduced into electrolysis cell (1). The cathode in electrolysis cell (1) is a
10 mixture of liquid copper and/or tin and possibly other sufficiently noble metals. As electrolyte a mixture of molten alkaline-earth chlorides and/or alkali chlorides is used to which some CaO is added at the start of the process. As anode graphite is used. The temperature at which the entire process takes place will typically lie between 500 and 1250 °C, depending on the precise
15 composition of the liquid electrolyte and the liquid cathode. When ZrO_2 contaminated with HfO_2 are added to electrolysis cell (1) and a sufficiently large potential difference between the anode and the cathode is applied, ZrO_2 contaminated with HfO_2 are reduced and will dissolve as their corresponding metals (Zr and Hf) into the molten metal cathode. At the anode CO is
20 produced.

The molten metal from electrolysis cell (1) is introduced into purification compartment (2) containing a mixture of molten alkaline-earth chlorides and/or alkali chlorides. Then a mixture of $\text{CuCl}_2/\text{SnCl}_2$ is added. The
25 metal Hf in the molten metal is now selectively oxidized and transported to the mixture of molten alkaline-earth chlorides and/or alkali chlorides. The molten alkaline-earth chlorides and/or alkali chlorides from purification compartment (2) are added to oxidation compartment (3). To oxidation compartment (3) oxygen is added (*viz.* pure or substantially pure oxygen) and the Hf in the
30 mixture of molten alkaline-earth chlorides and/or alkali chlorides is converted

into impure HfO_2 . The molten metal from purification compartment (2) is added to electro-refining cell (4).

In electro-refining cell (4) the liquid metal mixture from purification compartment (2) is used as liquid anode. As electrolyte a molten mixture of alkaline-earth chlorides and/or alkali chlorides can be used. At the start of the electro-refining process some ZrCl_4 or ZrCl_2 is made to be present in the electrolyte. As cathode a starting sheet of solid zirconium can be used. Consequently, from bottom to top in the electro-refining cell (4) there are present: as anode molten zirconium, copper and/or tin and possibly other sufficiently noble metals; as electrolyte a mixture of molten alkaline-earth chlorides and/or alkali chlorides with some ZrCl_4 or ZrCl_2 added to it; as cathode the starting sheet of solid zirconium. At the cathode very pure zirconium is produced.

Figure 2 schematically shows another processing route for producing purified zirconium. In this embodiment a feed of ZrCl_4 contaminated with HfCl_4 is introduced into electrolysis cell (1). In the embodiment of figure 2 the cathode and anode in electrolysis cell (1), purification compartment (2) and oxidation compartment (3) can be essentially the same and have the same function as in figure 1. The molten metal stream from compartment (2) is added to chlorination step (5), where Cl_2 gas is added. The Zr in the molten metal stream is converted to very pure ZrCl_4 which can be used in the Kroll process to produce very pure Zr.

Figure 3 schematically shows another processing route for producing purified zirconium. In this embodiment where a feed of ZrO_2 contaminated with HfO_2 is introduced into electrolysis cell (1). Purification compartment (2), oxidation compartment (3) and chlorination (5) can be essentially the same and have the same function as in the previous figures. The final product is very pure ZrCl_4 which can be used in the Kroll process to produce very pure Zr.

Figure 4 schematically shows another processing route for producing purified zirconium. In this embodiment a feed of ZrCl_4 contaminated with

HfCl₄ is introduced into electrolysis cell (1). Purification compartment (2), oxidation compartment (3) and electro-refining cell (4) can be essentially the same and have the same function as in the previous figures. At the cathode very pure zirconium is produced.

5 Figure 5 schematically shows another processing route for producing purified zirconium. In this embodiment a feed of Zr/Hf scrap is introduced into dissolution compartment (6). The scrap is dissolved into a mixture of liquid copper and/or tin and possibly other sufficiently noble metals in dissolution compartment (1). The molten metal from dissolution compartment (1) is
10 introduced into purification compartment (2). Purification compartment (2), oxidation compartment (3) and electro-refining cell (4) can be essentially the same and have the same function as in the previous figures. At the cathode very pure zirconium is produced.

 Figure 6 schematically shows another processing route for producing
15 purified zirconium. In this embodiment a feed of Zr/Hf scrap is introduced into dissolution compartment (6). The scrap is dissolved into a mixture of liquid copper and/or tin and possibly other sufficiently noble metals in dissolution compartment (1). The molten metal from dissolution compartment (1) is introduced into purification compartment (2). Purification compartment (2),
20 oxidation compartment (3) and chlorination (5) can be essentially the same and have the same function as in the previous figures. The final product is very pure ZrCl₄ which can be used in the Kroll process to produce very pure Zr.

 The liquid metal mixture obtained in the process in purification compartment (2) in the figures 1-6 may subsequently be subjected to a second
25 process essential similar to the process in purification compartment (2) in the figures 1-6 to further increase the Zr purity if required.

 Figure 7 schematically shows another processing route for purification of HfO₂ produced according to the processes described in figures 1-6. The first electrolysis cell (1), purification compartment (2), and electro-
30 refining (4) can be essentially the same and have the same function as in the

previous figures. A further electrolysis cell (7) is present, which operates similarly as the first electrolysis cell, but produces a molten metal stream that is circulated to further electrorefining cell (8) to produce at the cathode thereof very pure Hf.

5 Figure 8 schematically shows another processing route for purification of HfO_2 produced according to the processes described in figures 1-6. Electrolysis cell (1), purification compartment (2), chlorination (5) and further electrolysis cell (7) can be essentially the same and have the same function as in the previous figures. Further chlorination step (9) is employed to
10 produce very pure HfCl_4 , which can be used in the Kroll process to produce very pure Hf.

 In accordance with the present invention an impure liquid metal mixture of Zr/Hf and typically Cu and/or Sn which may comprise other sufficiently noble metals is subjected to purification step (2). The solution of
15 molten metals is contacted at a temperature typically between 500 and 1250 °C, *e.g.* at around 700 °C, with a molten salt mixture comprising a mixture of alkaline-earth chlorides and/or alkali chlorides and a halide of metal M^3Z , *e.g.* CuCl_2 . Instead of CuCl_2 or CuCl SnCl_2 or mixtures of these compounds may be used. Purification step (2) is preferably carried out under a
20 protective atmosphere, in particular under an atmosphere of inert gas (*viz.* a gas that does not, or not substantially react with any of the metals or the salts present), such as a noble gas, such as argon.

 The kinetics of the transfer of Hf from the molten metal phase to the salt phase are very fast resulting in an equilibrium composition for both
25 phases that it established almost instantaneously.

 The ratio Zr/Hf in the liquid metal mixture was found to have been increased strongly by this purification step (2), much more than one would expect based on the small difference in electronegativity for Hf (1.3 Pauling scale) and Zr (1.33 Pauling scale) .

In one embodiment, in the process of the present invention the mixture comprising hafnium and zirconium is obtained from an electrolytic process in which ZrO_2 and HfO_2 are contacted with an electrolyte. This electrolyte is in contact with a cathode so that electric charge can be transferred. This cathode is preferably a molten metal cathode. The electrolyte is also in mass exchanging and electric contact with an anode, preferably a carbon anode. By applying a suitable potential difference between cathode and anode Zr and Hf metal can be produced.

In another embodiment, the feed mixture comprising zirconium and hafnium can also be produced starting from impure ZrCl_4 , *viz.* ZrCl_4 contaminated with HfCl_4 .

The products from refining step (2) are a molten metal stream and a molten salt stream, both of which can be further processed, for instance by subjecting them to a further refining step (2).

The molten salt mixture obtained can be selectively oxidized. The oxidation product, which will contain both hafnium and zirconium, can be processed further with standard technology.

An electrorefining cell can be used to obtain high purity Zr as a product. In this electrorefining step (3) the liquid metal mixture, with relatively high concentration of zirconium, copper and/or tin and possibly other sufficiently noble metals is used as liquid anode. As electrolyte a molten salt mixture comprising a mixture of alkaline-earth chlorides and/or alkali chlorides can be used. At the start of the electro refining process the electrolyte will typically have to contain some zirconium chloride. As cathode a starting sheet of solid zirconium may be used. Thus, this cell comprises from bottom to top: molten zirconium with copper and/or tin and possibly other sufficiently noble metals as anode; as electrolyte a mixture of molten alkaline-earth chlorides and/or alkali chlorides with some zirconium chloride added to it; as cathode the starting sheet of solid zirconium. At the molten metal anode

zirconium atoms are oxidized to zirconium ions. At the solid cathode zirconium ions are reduced to zirconium metal.

The exchange current density at a elevated temperature at metals and particularly at liquid metals is extremely large. Due to this high exchange
5 current density at a elevated temperature it is believed that no or hardly any Zr^{3+} -ions or Zr^{4+} ions will be produced at the anode. When the potential difference applied between the anode and the cathode is not chosen too high, the copper and/or tin and possibly other sufficiently noble metals will not dissolve from the anode, because copper and the other metals chosen are more
10 noble than zirconium.

When the potential difference applied between the anode and the cathode is not chosen too high, reduction of the alkali- and alkaline-earth chlorides from the electrolyte to the corresponding metals at the cathode will not occur, because the alkali- and alkaline-earth metals are much less noble
15 than zirconium. The zirconium produced at the cathode in the electro refining process proposed will amply meet the requirements for application in nuclear industry. Because of the growth of zirconium at the cathode the distance between anode and cathode will decrease, as a result of which the current intensity will steadily increase.

20 By controlled moving upwards of the cathode during the electro refining process the current density can be kept constant. During the process the cathode is in fact slowly pulled from the electrolyte. The ohmic resistance of the electrolyte in combination with the current density applied lead to the production of heat. With a favorable geometry of the electro refining cell hardly
25 any additional energy will be needed to keep the electro refining cell at the required temperature. The temperature will generally lie between 500-1250 °C, depending on the precise composition of the liquid electrolyte and the liquid anode. Possible impurities in the liquid anode material can be removed at periodical intervals by *e.g.* selective oxidation, controlled cooling or
30 other treatment from the liquid anode material.

Alternatively, the liquid metal mixture, with relatively high concentration of zirconium, copper and/or tin and possibly other sufficiently noble metals is brought into contact with Cl_2 gas. Zirconium is preferably converted into gaseous ZrCl_4 . By standard technology this gaseous ZrCl_4 can be distilled for extra purification and used as feed for the Kroll process for the production of hafnium-low zirconium. In the Kroll process ZrCl_4 is reduced to metallic Zr using a suitable metal, *e.g.* magnesium.

The metal mixture comprising Zr and Hf that is used as feed in the process of the present invention can be obtained from numerous sources. For instance, it can be obtained starting from ZrO_2 -ore (contaminated with HfO_2), from ZrSiO_4 -ore (contaminated with HfSiO_4), and from combinations thereof.

For instance, an electrolysis cell can be used in which a mixture of liquid metals M^1 and M^2 , *e.g.* copper and tin and possibly other sufficiently noble metals are used as cathode. As electrolyte a molten salt, preferably CaCl_2 , can be used, possibly with alkali chlorides added to it, to which some CaO can be added at the start of the process. A graphite anode can be used.

The temperature is typically between 500 and 1250 °C, depending on the precise composition of the liquid electrolyte and the liquid anode. When a sufficiently large potential difference between the anode and the cathode is applied, Ca^{2+} ions will be reduced to calcium metal at the cathode, due to the high solubility of CaO in the electrolyte, which is the reason CaO is used instead of ZrO_2 alone. The calcium metal produced dissolves in the molten metal mixture as well as in the molten salt. At the anode the following reaction takes place: $\text{O}^{2-} + \text{C} \rightarrow \text{CO} + 2\text{e}^-$.

The CO produced escapes as a gas. The graphite anode is slowly consumed and can be renewed from time to time. The molten metal mixture and the molten salt mixture with dissolved calcium metal in both of them are subsequently brought into contact with solid ZrO_2 ore. The following reaction takes place: $\text{ZrO}_2 + 2\text{Ca} \rightarrow 2\text{CaO} + \text{Zr}$. ZrO_2 ore almost always contains some HfO_2 . This HfO_2 present in the ZrO_2 ore will behave in accordance with ZrO_2 .

The Zr and Hf produced dissolve in the liquid metal phase. The liquid metal mixture thus obtained can be used as feed for the separation process described above and in claim 1.

After reduction through calcium the contaminations in the ZrO_2 ore
5 will also end up in the liquid mixture of copper and/or tin and possibly other sufficiently noble metals. However, except for hafnium they are all more noble than zirconium, so that they do not present any direct problems in the electro-refining process. The CaO produced in the above reactions of ZrO_2 ore dissolves in the mixture of molten CaCl_2/CaO and possibly alkali chlorides. The entire
10 equipment is preferably put under a light overpressure of a noble gas, for example argon, in order to prevent air from penetrating. Instead of ZrO_2 ore ZrSiO_4 ore can also be used. When applying ZrSiO_4 the silicon produced during the reduction with calcium dissolves in the liquid metal mixture.

Alternatively, the feed mixture comprising zirconium and hafnium
15 can also be produced starting from relatively pure ZrCl_4 (*viz.* a mixture comprising mainly ZrCl_4 and HfCl_4 and relatively little other impurities, such as titanium) using an electrolytic set up.

In this embodiment a liquid mixture of two metals M^1 and M^2 as defined above is used as cathode in which are present possibly other
20 sufficiently noble metals. Molten salt, preferably CaCl_2 is used as an electrolyte. Preferably possibly alkali chlorides are present in the molten salt. As anode graphite is used. Without wishing to be bound by theory, it is believed that when a sufficiently large potential difference between the anode and the cathode is applied, Ca^{2+} ions will be reduced to calcium metal at the
25 cathode.

This calcium metal produced at the cathode dissolves in the mixture of liquid copper and/or tin and possibly other sufficiently noble metals as well as in the molten mixture of CaCl_2 and possibly alkali chlorides. However when no calcium is present as an intermediate, the process may still work.

30 At the anode the following reaction takes place: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$.

The produced Cl_2 escapes as a gas. It can be used to produce the required ZrCl_4 from ZrO_2 -ore or from ZrSiO_4 ore in accordance with existing technology.

The molten metal mixture and the molten salt mixture are
5 subsequently brought into contact with gaseous ZrCl_4 . The following reaction takes place: $\text{ZrCl}_4 + 2\text{Ca} \rightarrow \text{Zr} + 2\text{CaCl}_2$. The HfCl_4 present in the ZrCl_4 will behave accordingly. Instead of gaseous ZrCl_4 also solid ZrCl_2 dissolved in molten salt can be used in accordance with the present invention.

The produced zirconium and hafnium dissolve in the liquid mixture
10 of copper and/or tin and possibly other sufficiently noble metals. It can be used as feed for the refining processes for zirconium as described above.

The CaCl_2 released in the above reaction mixes with the molten mixture of CaCl_2 and possibly alkali chlorides. The temperature at which the entire process should take place will lie between 500 en 1200 °C, depending on
15 the precise composition of the liquid electrolyte and the liquid anode. Moreover, the entire equipment should be put under a light overpressure of a noble gas, for instance argon, in order to prevent air from penetrating.

Alternatively, a feed for the process of the present invention can be provided starting from Zr/Hf scrap.

20 The scrap can be simply dissolved in the liquid mixture metals as described above. The resulting mixture comprising hafnium and zirconium can be processed as described above.

An important advantage of the present invention is the high efficiency for removing Hf from Zr. This is further illustrated by the following
25 examples which are not intended to limit the scope of the present invention.

Examples

Equilibrium experiments

30 *Raw materials*

Laboratory grade chemicals were used for the equilibrium experiments. Metallic powders: Zr, Hf, Cu and Sn had a purity of higher than 99.9%. Chloride salts: CuCl₂, NaCl and CaCl₂ had a purity of 99.9%.

Master alloy and salt preparation

5 Zr and Hf containing Sn-Cu master alloy was prepared in an alumina crucible under purified argon atmosphere with pre-melted NaCl-CaCl₂ salt mixture at 850°C for 6 hours. The master salt mixture was prepared with NaCl, CaCl₂ and CuCl₂ powders. After mixing the salt mixture was fused at 750 °C for 4 hours, and then cooled to room temperature. The CuCl₂ content
10 in the master salt was prepared to be 2.956 wt%.

Equilibrium experiments

For the equilibrium experiments, a well determined mixture of master salt and master alloy was charged in the alumina crucible, and placed
15 in a carbolite electrical resistant tube furnace under purified argon atmosphere.

The major reaction was:



Theoretically, to react with 1 g of Hf in the metal phase, 1.596 g CuCl₂ is required. The equilibrium experiments were conducted under various controlled conditions. The two major factors influencing the salt and alloy
25 reaction equilibrium have been examined: temperature (750 °C and 850 °C), and stoichiometric ratio (1, 2 and 3) of the added CuCl₂ containing salt to the Hf containing alloy. The equilibrium time was maintained for 4 hours. After the equilibrium tests, the composition of the metal phase was analyzed by an inductively coupled plasma (ICP) spectrometer.

Results and discussion

Table 1 lists the conditions of the equilibrium experiments, and the experimental results. The equilibrium tests gave very positive results, as shown in Figures 9 and 10. The Hf removal efficiency from Zr varies from 76.0% to 99.9%, and the Hf to Zr ratio is lowered from 0.128 to 0.0002 with a removal factor of 640 ($0.128/0.0002=640$) at 850 °C with stoichiometric ratio of $\text{CuCl}_2/\text{Hf} = 1$.

Table 1: Experimental conditions and results (the reacted samples are named after the reaction temperature and the stoichiometric ratio of CuCl_2 in salt to Hf in master alloy)

Test	Code	Temperature °C	Stoichiometric ratio of CuCl_2/Hf	Zr wt%	Hf wt%	Hf/Zr	Hf removal efficiency, %
---	Master alloy	---	---	1.071	0.1374	0.128	---
No. 1	750-S/M-1	750	1	1.050	0.01408	0.0134	89.8
No. 2	750-S/M-2	750	2	1.299	0.03296	0.0254	76.0
No. 3	750-S/M-3	750	3	1.214	0.01454	0.0120	89.4
No. 4	850-S/M-1	850	1	0.7737	0.000162	0.0002	99.9
No. 5	850-S/M-2	850	2	1.146	0.001996	0.0017	98.5

The contents of Sn and Cu in the reacted metal phase did not have a significant change. However, Hf has been removed from Zr with a high efficiency of 99.9% at 850°C with one stoichiometric ratio of added CuCl_2 in the master salt to the Hf amount in the master alloy ($\text{S/M}=1$). Figure 10 shows the Hf removal efficiency at 750°C and 850 °C with varying stoichiometric ratios of added CuCl_2 containing salt, and the temperature has significant positive effect on the Hf removal efficiency. In addition, Cu in the salt after reaction was detected generally to be very low according to the ICP analysis on the reacted salt samples.

Based on these experimental results and observations, the production and refining process of the present invention is proved to be technically feasible.

Claims

1. Process for separating a mixture comprising hafnium and zirconium, comprising the steps of:
 - providing a molten metal phase comprising a first metal M^1 and a second metal M^2 ;
 - 5 - providing a molten salt phase comprising at least one metal halide M^3Z , wherein M^3 is a metal that is less electropositive than zirconium and hafnium, and one or more salts of one or more metals M^4 , wherein M^4 is a metal from Group 1 or Group 2 of the Periodic Table;
 - feeding said mixture comprising hafnium and zirconium to said molten metal
10 phase; and
 - contacting said molten metal phase and said molten salt phase, whereby at least part of said hafnium is transported from said molten metal phase to said molten salt phase.
2. Process according to claim 1, wherein at least a part of the amount
15 M^1 and M^3 present are the same metals.
3. Process according to any of the previous claims, wherein at least a part of the amount M^2 and M^3 present are the same metals.
4. Process according to any of the previous claims, wherein no zirconium salt is added to said molten salt phase, and wherein preferably said
20 molten salt phase is substantially free from zirconium salt.
5. Process according to any of the previous claims, wherein M^1 and M^2 are each independently selected from Cu, Sn, Ag, Sb, Zn, Pb, Bi, Fe, Ni, Cd, Si and Co, wherein preferably M^2 is a metal that lowers the melting point of M^1 .
6. Process according to any of the previous claims, wherein M^1 is Cu
25 and M^2 is Sn.
7. Process according to any of the previous claims, wherein said salt of M^4 is a halide or a mixture of halides.

8. Process according to any of the previous claims, wherein M^4 is selected from Na, K, Ba, Sr and Ca, and wherein preferably said salt of M^4 is a combination of a chloride or fluoride of Ca, Na and/or K, more preferably $CaCl_2$.
- 5 9. Process according to any of the previous claims, wherein the metals in said molten metal phase are present in a mutual molar ratio that is substantially the same as the mutual molar ratio of the metals M^3 in said molten salt phase.
10. Process according to any of the previous claims, wherein the amount
10 of M^3Z that is added to said molten salt phase is proportional to the amount of Hf to be removed from said mixture comprising Hf and Zr.
11. Process according to any of the previous claims, wherein the temperature of said molten metal and said molten salt is kept at a temperature of between 500-1250 °C, preferably of 700-1000 °C.
- 15 12. Process according to any of the previous claims, wherein said mixture comprising hafnium and zirconium is obtained from an electrolytic process in which a zirconium and hafnium source selected from ZrO_2 contaminated with HfO_2 , $ZrSiO_4$ contaminated with $HfSiO_4$ and combinations thereof is contacted with an electrolyte, which is in electric and mass
20 exchanging contact with a molten metal cathode, and which electrolyte is in electric and mass exchanging contact with an anode, whereby zirconium and hafnium ions from said zirconium and hafnium source are reduced to Zr and Hf metal and transported to said molten metal phase, at least part of which is drawn off to provide said mixture comprising hafnium and zirconium.
- 25 13. Process according to any of the previous claims, wherein said mixture comprising hafnium and zirconium is obtained from an electrolytic process in which $ZrCl_4$ contaminated with $HfCl_4$ is fed to an electrolysis cell.
14. Process according to any of the previous claims, wherein at least
30 part of said molten metal phase is drawn off and fed to a refining step, wherein said molten metal phase forms an anode and is contacted with a refining

electrolyte, which is in electric contact with a cathode, comprising metallic Zr and which refining electrolyte is in mass exchanging and electric contact with said molten metal phase, , whereby metallic Zr is deposited on said cathode.

15. Process according to any of the previous claims, wherein at least
5 part of said molten salt phase is drawn of and subjected to a refining step to produce a stream rich in Hf.

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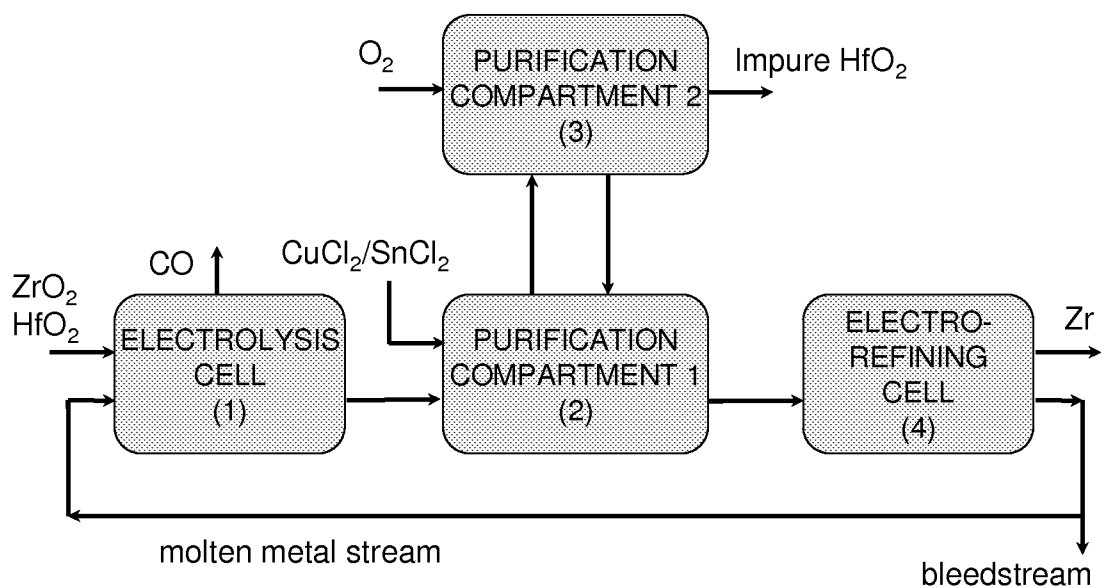


Figure 1

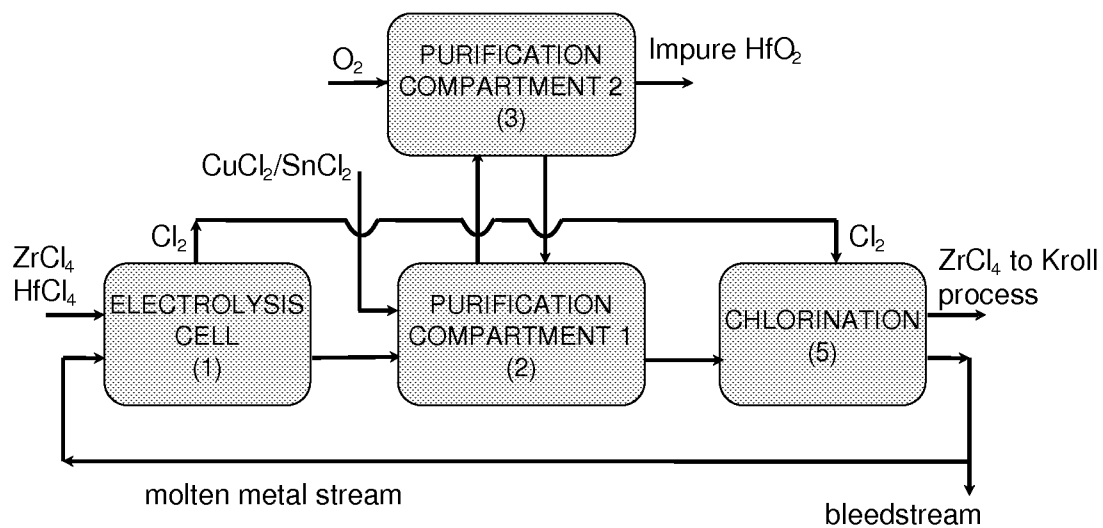


Figure 2

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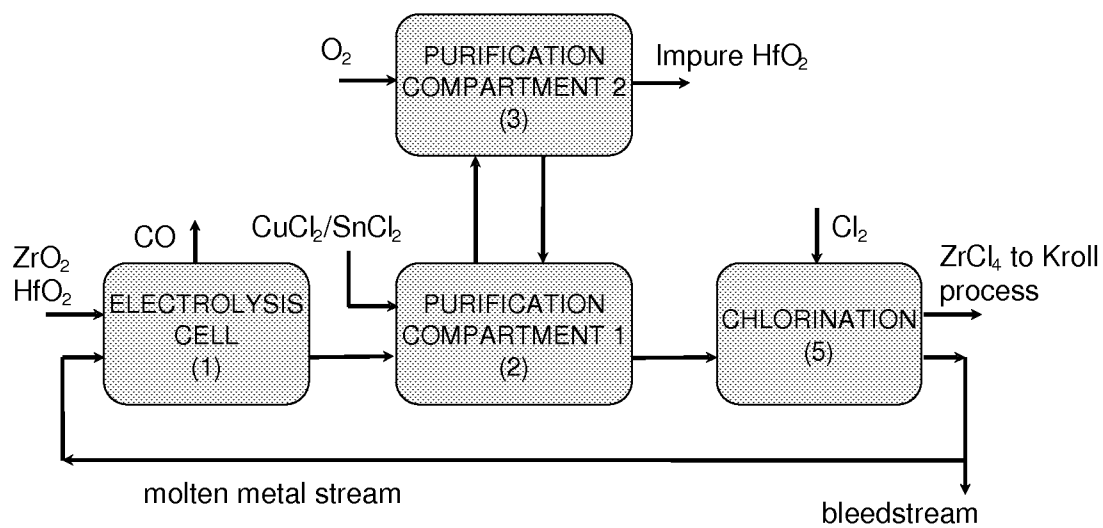


Figure 3

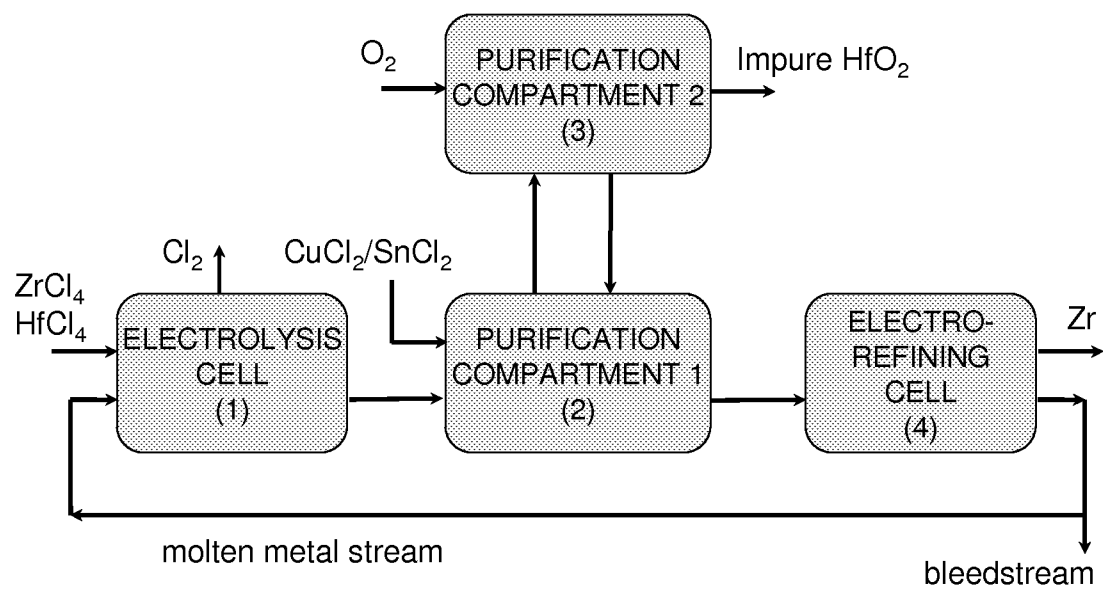


Figure 4

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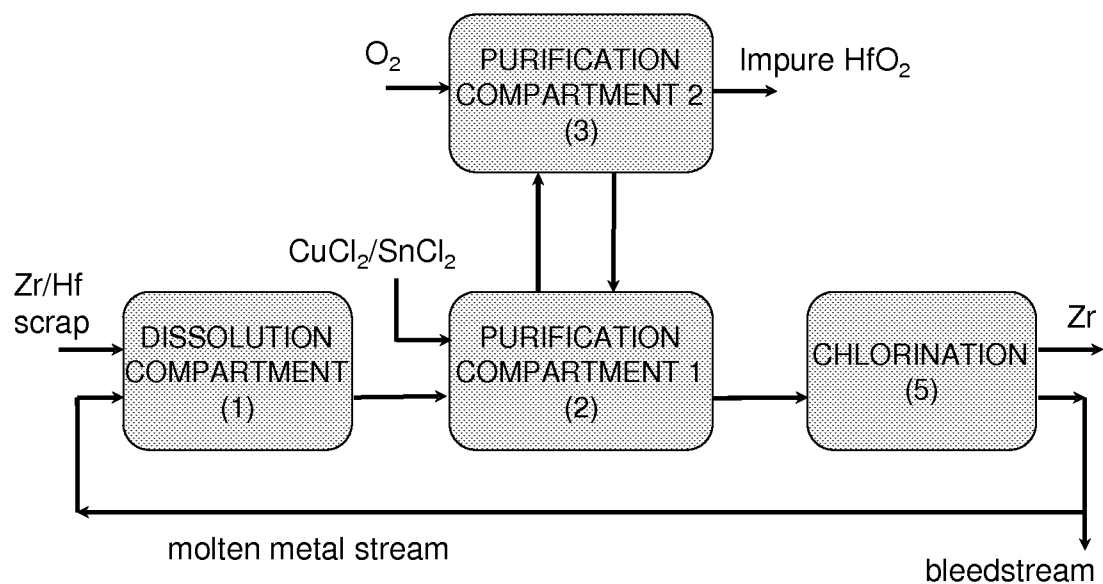


Figure 5

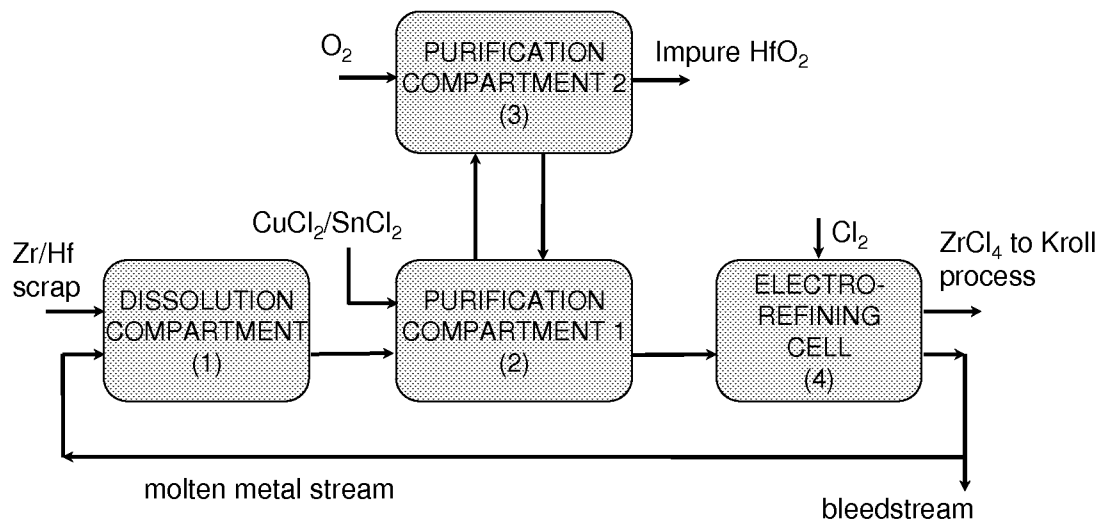


Figure 6

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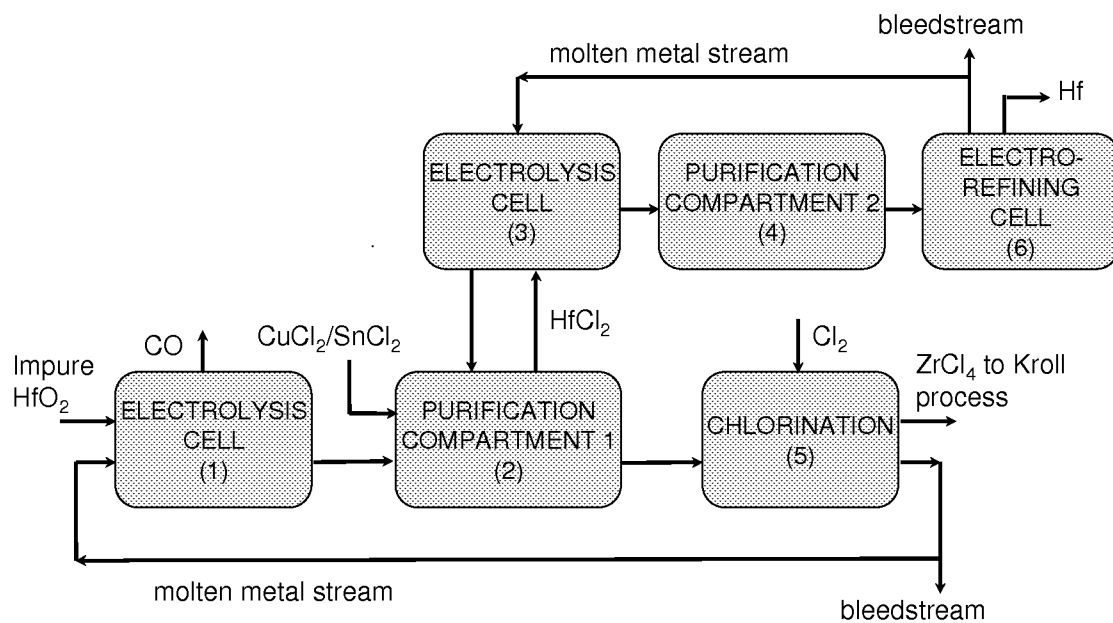


Figure 7

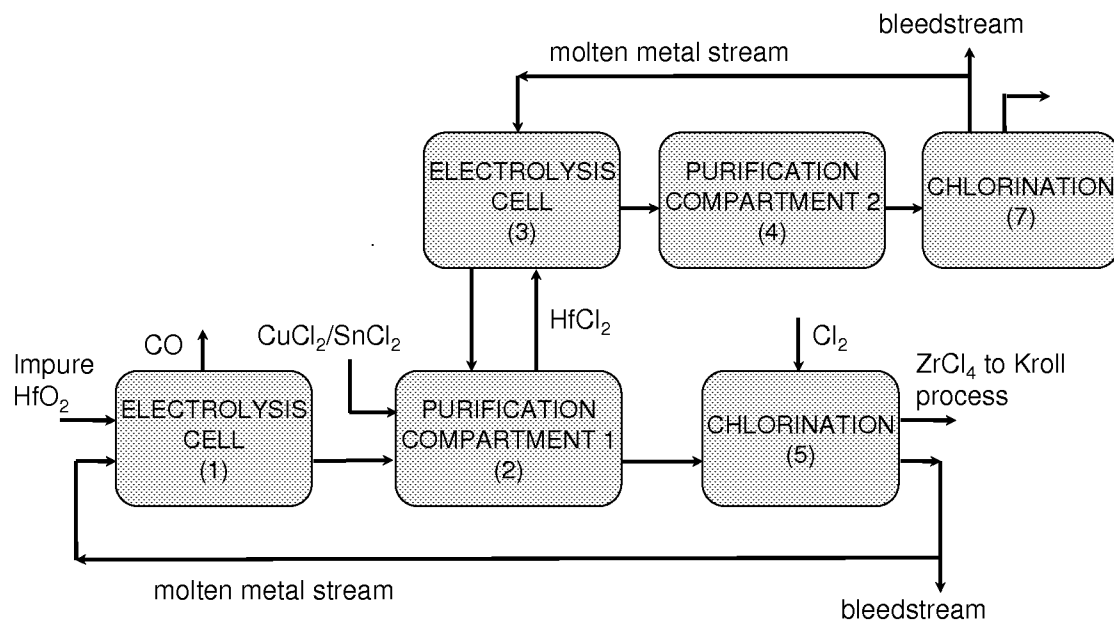


Figure 8

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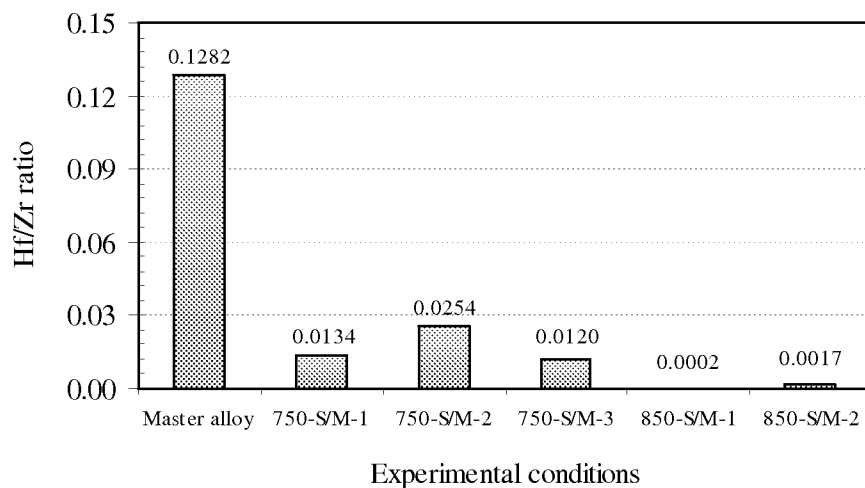


Figure 9. Hafnium to zirconium ratio under various experimental conditions

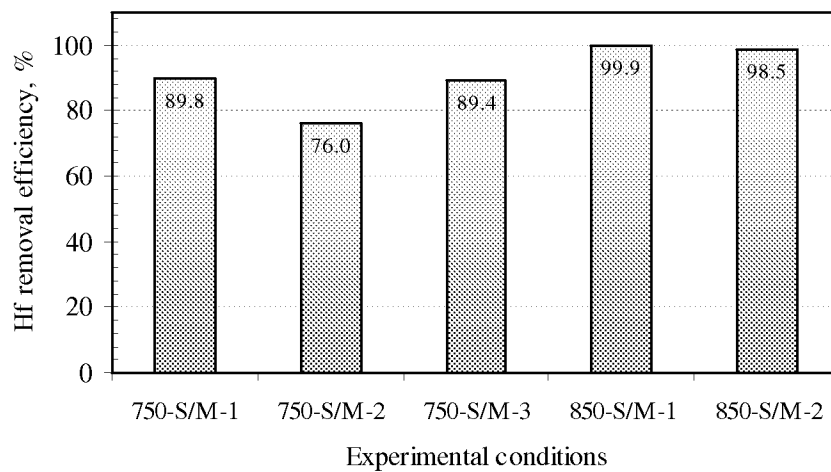


Figure 10. Hafnium removing efficiency under various experimental conditions

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2010/050289

A. CLASSIFICATION OF SUBJECT MATTER
INV. C22B34/14 C25C3/26
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C25C C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 072 506 A (MEGY JOSEPH ALLEN) 7 February 1978 (1978-02-07) cited in the application column 2, line 64 - column 3, line 10; claims 1-3,6	1-15
A	J.A. MEGY, H. FREUND: "The Separation of Zirconium and Hafnium in a Molten Salt - Molten Zinc System" METALLURGICAL TRANSACTIONS B, vol. 10B, September 1979 (1979-09), pages 413-421, XP009124561 ISSN: 1073-5615 the whole document	1-15
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

5 August 2010

Date of mailing of the international search report

20/08/2010

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Hammerstein, G

INTERNATIONAL SEARCH REPORT

International application No

PCT/NL2010/050289

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MALLIKARJUNAN R ET AL: "Pyrometallurgical processes for the separation of hafnium from zirconium" BULLETIN OF MATERIALS SCIENCE, INDIAN ACADEMY OF SCIENCES, IN, vol. 12, September 1989 (1989-09), pages 407-434, XP009124559 ISSN: 0250-4707 pages 427-428 -----	1-15

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Information on patent family members

International application No

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