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

(11) Publication number: 0 134 643
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 84304460.3

(22) Date of filing: 29.06.84

(51) Int. Cl.⁴: **C 22 B 34/10**

(30) Priority: 08.07.83 JP 123193/83
08.07.83 JP 123194/83

(43) Date of publication of application:
20.03.85 Bulletin 85/12

(84) Designated Contracting States:
DE FR GB

(71) Applicant: Solex Research Corporation of Japan
23-9, Maruyama-cho
Shibuya-ku Tokyo(JP)

(72) Inventor: Watanabe, Morio
8-23-22, Minamitsukaguchi-cho
Amagasaki-shi Hyogo-ken(JP)

(72) Inventor: Nishimura, Sanji
13-8, Fukakusa Nanmei-cho Fushimi-ku
Kyoto-shi Kyoto-fu(JP)

(74) Representative: Brewer, Leonard Stuart et al,
Sanderson & Co. 97 High Street
Colchester Essex CO1 1TH(GB)

(54) Preparing metallic zirconium, hafnium or titanium.

(57) Metallic zirconium, hafnium or titanium is prepared by bringing a fluorine-containing compound thereof into contact with heated metallic aluminium or magnesium, to convert the fluorine-containing compound into the corresponding metal.

Croydon Printing Company Ltd.

PREPARING METALLIC ZIRCONIUM, HAFNIUM OR TITANIUM

The present invention relates to the preparation of metallic zirconium, metallic hafnium and metallic titanium.

So far, metallic zirconium (Zr) and metallic hafnium (Hf) have been produced by reducing their chlorides with metallic magnesium or sodium in a stream of an inert gas. Since metallic sodium is hazardous, metallic magnesium has been used more often as the reducing agent. Metallic titanium has generally been produced from TiO_2, by chlorinating it in the presence of carbon to produce $TiCl_4$ as an intermediate, and reducing this intermediate by contact with metallic magnesium or sodium to obtain metallic titanium.

These conventional processes, however, involve rather rather complicated operations for producing metallic zirconium or metallic hafnium and a high cost in consumption of metallic magnesium or sodium. In the preparation of metallic titanium, sources of raw material TiO_2 are limited since the material is required to have a low content of impurities, and a complex process for purifying the $TiCl_4$ intermediate is needed before metallic titanium is produced. In addition, the preparation of titanium is accompanied by troublesome management in order to attain the desired end. The high cost involved when metallic magnesium or sodium is used for the reduction necessarily raises the production cost of metallic titanium. This is the chief reason why application of titanium is not widely developed despite the excellent properties of the metal.

The present invention provides a new, improved, process which is intended to overcome such drawbacks of the previous processes. The invention provides a process for preparing metallic zirconium, hafnium or titanium, which process comprises bringing a fluorine-containing compound of zirconium, hafnium or titanium into contact with heated metallic aluminium or magnesium, to convert the fluorine-containing compound into the corresponding metal.

In this invention, metallic Zr, Hf and Ti are prepared from fluorine-containing compounds of the metals, instead of from their chlorides. The fluorine-containing compounds are better starting materials. Crystals of them are prepared more easily. The fluorine-containing compounds provide more easily purifiable crystals than do the corresponding chlorides. In addition, metallic aluminium can be used as the reducing agent in the present invention. Furthermore, the fluorine necessary for preparing the fluorine-containing compounds as intermediates can be recirculated in the process.

In the present process, a fluorine-containing compound of zirconium, hafnium or titanium reacts with heated metallic aluminium or magnesium to convert the fluorine-containing compound into the corresponding metal. The reaction should naturally not be conducted in the presence of material which mars the reaction. Oxygen, for example air, mars the reaction and hence should be avoided. The reaction can be conducted in the presence of an inert gas or a reducing gas. Alternatively, the reaction can be conducted "in vacuum", i.e. with no other gas being present besides any from the fluorine-containing compound and the aluminium or magnesium. Preferably, the fluorine-containing compound in the reaction is gaseous. The compound may contact initially as a solid with the aluminium or magnesium and then be heated to make it gaseous. In a preferred embodiment, the reaction is conducted with the compound being gaseous and being in an inert gas or a reducing gas.

To prepare zirconium or hafnium, the aluminium or magnesium is generally heated to a temperature above 400°C. To prepare titanium, the aluminium or magnesium is generally heated to a temperature above 220°C.

The fluorine-containing compound can be for instance $(NH_4)_2ZrF_6$, $(NH_4)_2HfF_6$, $(NH_4)_2TiF_6$, TiF_4, ZrF_4, HfF_4 or K_2TiF_6.

Gaseous fluorine-containing compound is generally produced by heating solid fluorine-containing compound.

The fluorine-containing compound is preferably produced by extracting a zirconium, hafnium or titanium compound into an organic solvent, and bringing the solution into contact with an aqueous solution containing at least one of F^-, NH_4^+ and K^+ to extract into the aqueous phase zirconium, hafnium or titanium in the form of a fluorine-containing compound thereof. The fluorine-containing compound can then be crystallized from the aqueous solution.

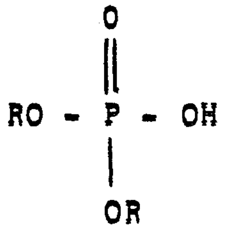
The organic solvent can be regarded as comprising an extracting agent, which can be in admixture with a diluent.

In a preferred aspect, the fluorine-containing compound is produced by extracting a zirconium, hafnium ortitanium compound into a solvent comprising at least one extracting agent selected from the group consisting of (a) alkylphosphoric acids, (b) alkylarylphosphoric acids, (c) alkylamines, (d) neutral phosphoric acid esters and (e) ketones, and bringing the solution into contact with an aqueous solution containing at least one of F^-, NH_4^+ and K^+ to extract into the aqueous phase zirconium, hafnium or titanium in the form of a fluorine-containing compound thereof. The solvent can comprise the extracting agent, i.e. one or more of (a), (b), (c), (d) and (e), diluted with a diluent, particularly petroleum hydrocarbon. In a particularly preferred embodiment of this aspect, the solvent comprises the extracting agent diluted with petroleum hydrocarbon, the aqueous solution contains NH_4^+, and metallic zirconium or hafnium is prepared.

In another particularly preferred embodiment of the present process, metallic titanium is prepared and the fluorine-containing compound of titanium is produced by extracting a titanium compound into a solvent comprising (1) at least one extracting agent selected from the group consisting of (A) alkylphosphoric acids, (B) alkylarylphosphoric acids, (C) carboxylic acids, (D) oximes and (E) neutral phosphoric acid esters, and (2) petroleum hydrocarbon as diluent, and bringing the solution into contact with an aqueous solution containing at least one of F^-, NH_4^+ and K^+ to extract into the aqueous phase titanium in the form of a fluorine-containing compound thereof.

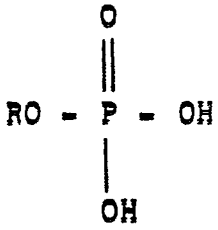
The alkylphosphoric acids which can be employed as extracting agent in the present invention are preferably selected from the group consisting of the following compounds:

(a)



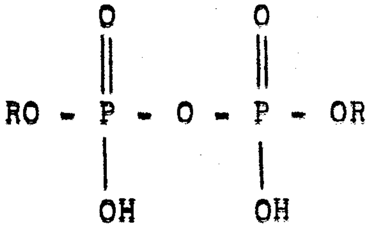
$\mathrm{RO-P(=O)(OR)-OH}$

(b)



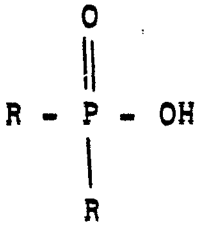
$\mathrm{RO-P(=O)(OH)-OH}$

(c)



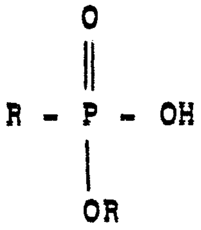
$\mathrm{RO-P(=O)(OH)-O-P(=O)(OH)-OR}$

(d)



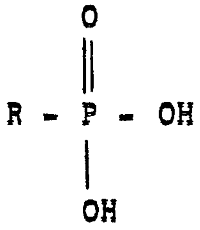
$\mathrm{R-P(=O)(R)-OH}$

(e)



$\mathrm{R-P(=O)(OR)-OH}$

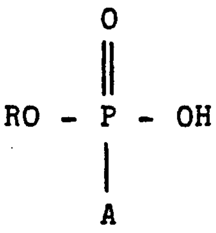
(f)



$\mathrm{R-P(=O)(OH)-OH}$

(In the formulae, R represents an alkyl group generally containing 4 to 22 carbon atoms). The compound D_2EHPA (di-2-ethylhexylphosphoric acid) referred to in the Examples below is the compound of group (a) where R represents C_8H_{17}.

The alkylarylphosphoric acids which can be employed in the present invention are preferably selected from the compounds of the following general formula:

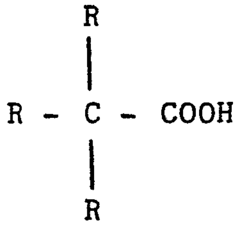


$$RO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle A}{|}}{P}}-OH$$

(In the formula, R represents an alkyl group containing generally 4 to 14 carbon atoms and A represents an aryl group, for instance a phenyl, tolyl, or xylyl group).

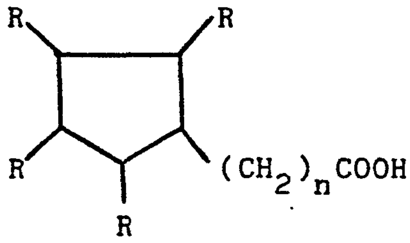
The carboxylic acids which can be employed as extracting agent in this invention are preferably selected from the group consisting of the compounds of the following general formulae:

(a)



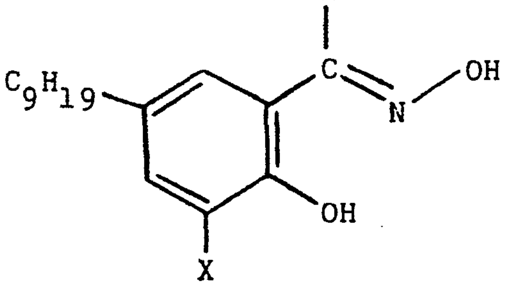
$$R-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}-COOH$$

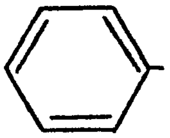
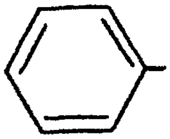
(b)



(In the formulae, R represents an alkyl group having 4 to 18 carbon atoms).

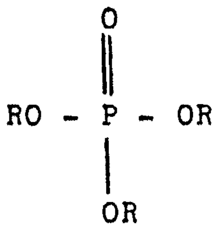
An example of an oxime which can be employed as extracting agent is shown below:



(In the formula, R represents H-, CH_3-,  or  CH_2-; and X represents a halogen atom such as Cl or an H atom).

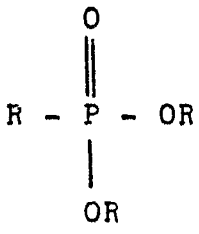
The neutral phosphoric acid esters which can be employed in the present invention are preferably selected from the following compounds:

(a)



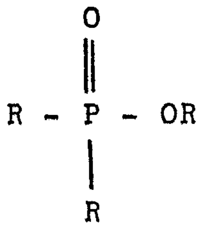
$RO-\underset{\underset{OR}{|}}{\overset{\overset{O}{\|}}{P}}-OR$

(b)



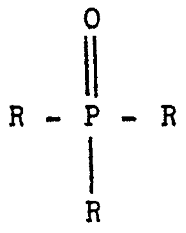
$R-\underset{\underset{OR}{|}}{\overset{\overset{O}{\|}}{P}}-OR$

(c)



$R-\underset{\underset{R}{|}}{\overset{\overset{O}{\|}}{P}}-OR$

(d)



$R-\underset{\underset{R}{|}}{\overset{\overset{O}{\|}}{P}}-R$

(In the formulae, R represents an alkyl group having 4 to 22 carbon atoms). TBP (tributyl phosphate) referred to in the Examples is the compound of formula (a) where $R = C_4H_9$.

The alkylamines which can be employed in this invention are preferably selected from the following groups of compounds:

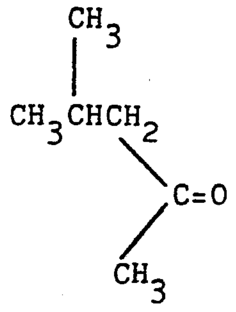
Primary amines : Represented by RNH_2, where R represents an alkyl group of 4 to 22 carbon atoms.

Secondary amines : Represented by R_2N^- or R_2NH, where R represents an alkyl group of 4 to 22 carbon atoms.

Tertiary amines : Represented by R_3N or R_3NH^+, where R represents an alkyl group of 4 to 22 carbon atoms.

TOA (trioctylamine) referred to in the Examples is the tertiary amine where $R = C_8H_{17}$.

An example of a ketone which can be employed in this invention has the formula:



Cyclohexanone, $(C_6H_{10})O$, is also a preferred compound.

The most frequently used diluents in this invention are petroleum hydrocarbons, but aromatic and aliphatic hydrocarbons and mixtures thereof can also be used with success. Further, a mixture of various hydrocarbons such as kerosene is often used.

In addition, a higher alcohol generally containing an alkyl group of 4 to 24 carbon atoms can be employed to improve the quality of the products. The higher alcohol is generally present in a proportion ranging from 0 to 30% (by volume). The concentration of the extracting agent should be chosen according to the nature of the solution to be treated as well as of the suspected impurities, the concentration of the metal of interest and of impurities, and also according to the chemical species to be extracted. The concentration of the extracting agent is generally, however, in the range 2 to 100% (by volume).

The metallic aluminium and metallic magnesium for use as reducing agents may be in the form of a liquid or gas. The metallic Zr, Hf or Ti can be produced by bringing gaseous fluorine-containing compound thereof into contact with the metallic aluminium or magnesium in a stream of an inert gas or a reducing gas or in vacuum.

The inert gas which can be used to maintain the reaction conditions in the present process may be for example argon, helium or nitrogen, and the reducing gas for the same purpose may be for example H_2, CO or a number of hydrocarbons whose molecular formula is C_nH_m.

The fluoride in the aluminium fluoride or magnesium fluoride produced as by-product in the present process can be recovered and reused. Thus, it can be recycled for use in the aqueous solution discussed above for producing the fluorine-containing compound of zirconium, hafnium or titanium. The aluminium fluoride or magnesium fluoride can be reacted for instance with steam to produce HF which can be recycled for use in the aqueous solution.

The invention is illustrated by the accompanying drawings, in which:

Fig. 1 is a flow sheet illustrating the basic process of the invention;

Fig. 2 is a more elaborate flow sheet which also illustrates the production of the starting material; and

Fig. 3 is a yet more elaborate flow sheet which also illustrates the recovery and re-use of fluoride after the basic process.

The invention will now be described with reference to the accompanying drawings, but it will be appreciated that discussion is applicable generally.

The flow sheet of Fig. 1 shows the basic process for producing Zr, Hf or Ti. The fluorine-containing compound (A) of Zr, Hf or Ti is introduced into a reactor (C) where metallic aluminium or magnesium is heated, preferably above 400°C for zirconium and hafnium, and preferably above 220°C for titanium, in a stream of an inert or reducing gas or in vacuum. In the reactor, metallic zirconium, metallic hafnium or metallic titanium is prepared according to reactions such as are expressed by the following equations:

$$\mathrm{ZrF_4} + 1\tfrac{1}{3}\mathrm{Al} \rightleftharpoons \mathrm{Zr}\downarrow + 1\tfrac{1}{3}\mathrm{AlF_3}\uparrow \;\ldots\ldots\ldots\ldots\ldots\; (1)$$

$$\mathrm{HfF_4} + 2\mathrm{Mg} \rightleftharpoons \mathrm{Hf}\downarrow + 2\mathrm{MgF_2}\uparrow \;\ldots\ldots\ldots\ldots\ldots\; (2)$$

$$\mathrm{(NH_4)_2ZrF_6} + 2\mathrm{Mg} \rightleftharpoons \mathrm{Zr}\downarrow + 2\mathrm{MgF_2}\uparrow + 2\mathrm{NH_4F}\uparrow \;\ldots\; (3)$$

$$\mathrm{(NH_4)_2HfF_6} + 1\tfrac{1}{3}\mathrm{Al} \rightleftharpoons \mathrm{Hf}\downarrow + 1\tfrac{1}{3}\mathrm{AlF_3}\uparrow + 2\mathrm{NH_4F}\uparrow \;\ldots\; (4)$$

The fluorine-containing compounds of Zr and Hf are not limited to those shown in equations (1) to (4).

As shown in the equations above, AlF_3, MgF_2, HF and NH_4F (D) are produced as by-products in addition to the metallic zirconium or metallic hafnium. The former compounds can be led outside the system in a gaseous form, depending on the operating conditions of the reactor (C). If they are retained in the reactor, they can be removed by washing with water or dilute aqueous acids or by heating in a vacuum furnace.

Metallic titanium can be prepared by the reaction with metallic aluminium according to the following equations:

$$\mathrm{TiF_4} + 1\tfrac{1}{3}\mathrm{Al} \rightleftharpoons \mathrm{Ti}\downarrow + 1\tfrac{1}{3}\mathrm{AlF_3}\uparrow \;\ldots\ldots\ldots\ldots\ldots\; (5)$$

$$\mathrm{(NH_4)_2TiF_6} + 1\tfrac{1}{3}\mathrm{Al} \rightleftharpoons \mathrm{Ti}\downarrow + 1\tfrac{1}{3}\mathrm{AlF_3}\uparrow + 2\mathrm{NH_4F}\uparrow \;\ldots\; (6)$$

$$\mathrm{K_2TiF_6} + 1\tfrac{1}{3}\mathrm{Al} \rightleftharpoons \mathrm{Ti}\downarrow + 1\tfrac{1}{3}\mathrm{AlF_3}\uparrow + 2\mathrm{KF}\uparrow \;\ldots\ldots\; (7)$$

By-products such as AlF_3, KF and NH_4F (D) are led outside the reactor (C) in gaseous form to separate them from Ti. Alternatively, depending on the operating conditions, the metallic titanium is washed with water or dilute aqueous acid to remove the by-products.

Metallic titanium (E) can be obtained from fluorine-containing compounds of titanium (A) by the reaction with metallic magnesium (B), usually heated at a temperature above 220°C, as shown in the following equations:

$$TiF_4 + 2Mg \rightleftharpoons Ti\downarrow + 2MgF_2\uparrow \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

$$(NH_4)_2TiF_6 + 2Mg \rightleftharpoons Ti\downarrow + 2MgF_2\uparrow + 2NH_4F\uparrow \quad \ldots\ldots \quad (9)$$

$$K_2TiF_6 + 2Mg \rightleftharpoons Ti\downarrow + 2MgF_2\uparrow + 2KF\uparrow \quad \ldots\ldots\ldots\ldots \quad (10)$$

The flow sheet of Fig. 2 illustrates the process in which the fluorine-containing compound of Zr, Hf or Ti is produced as starting material. An organic solvent (F) extracting and containing Zr, Hf or Ti is led to a stripping stage (G), where Zr, Hf or Ti in the organic phase is transferred to an aqueous phase (H) by being contacted with an aqueous solution (E) which contains one or more of NH_4^+ and F^- for Zr and Hf and of NH_4^+, F^- and K^+ for Ti, to obtain fluorine-containing compounds of these metals. This may be illustrated by the following equations:

$$R_4.Zr + 4HF \rightleftharpoons 4R.H + ZrF_4 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

$$R_4.Hf + 4NH_4HF_2 \rightleftharpoons 4R.H + (NH_4)_2HfF_6 + 2NH_4F \quad . \quad (12)$$

$$H_2ZrF_6.nTBP + 2NH_4F \rightleftharpoons (NH_4)_2ZrF_6 + nTBP + 2HF \quad (13)$$

$$(R_3NH)_2ZrO(SO_4) + 4NH_4HF_2 \rightleftharpoons (NH_4)_2ZrF_6 + 2R_3NH.F + (NH_4)_2SO_4 + H_2O \quad \ldots\ldots (14)$$

$$R_4.Ti + 4HF \rightleftharpoons 4R.H + TiF_4 \quad \ldots\ldots (15)$$

$$H_2TiF_6.nTBP + 2NH_4F \rightleftharpoons nTBP + (NH_4)_2TiF_6 \quad \ldots\ldots (16)$$

$$R_4.Ti + 4NH_4HF_2 \rightleftharpoons 4R.H + (NH_4)_2TiF_6 + 2NH_4F \quad \ldots (17)$$

$$R_4.Ti + 4KHF_2 \rightleftharpoons 4R.H + K_2TiF_6 + 2KF \quad \ldots\ldots (18)$$

where R.H is an extracting agent having an H-type exchanging group, and TBP represents tributyl phosphate.

Regenerated organic solvent (K) is circulated again to the extraction stage. The Zr, Hf or Ti transferred to the aqueous medium is deposited as crystals such as $(NH_4)_2ZrF_6$, $(NH_4)_2HfF_6$, TiF_4, $(NH_4)_2TiF_6$ or K_2TiF_6, and is removed from the aqueous medium by filtration (J). The fluorine-containing compound of Zr, Hf or Ti obtained (A) is treated as shown in Fig. 1 to produce metallic zirconium, hafnium or titanium.

Fig. 3 is a flow-sheet of the present invention which includes a procedure for treating AlF_3, MgF_2 and NH_4F (D) by-products from the reduction of the fluorine-compounds of Zr, Hf and Ti by means of metallic magnesium and aluminium. The route from the organic solvent (F) which contains Zr, Hf or Ti as a result of extraction to the reactor (C) is as shown in Fig. 2. AlF_3 or MgF_2 (D) from the reactor (C) is transferred to the decomposition stage (M), where it is converted into Al_2O_3 or MgO (N) by the action of steam or air, as illustrated by the following equations:

$$2AlF_3 + 3H_2O \text{ (steam)} \rightleftharpoons Al_2O_3 + 6HF \text{ .... } (19)$$

$$MgF_2 + H_2O \text{ (steam)} \rightleftharpoons MgO + 2HF \text{ .... } (20)$$

The HF (Q) produced in the oxidation reactions is introduced for recovery into the absorption stage (P) where a NH_4F- and NH_4HF_2-containing solution circulates, the solution acting as stripper for Zr, Hf or Ti.

As the reactor (C) of the present invention, those of various forms can be used including conventional closed type electric furnaces or external heating furnaces having a double structure (upright, horizontal or rotational).

The invention is illustrated by the following Examples.

Example 1

Crystals of $(NH_4)_2ZrF_6$ were obtained by a process in which zirconium extracted with a mixed organic solvent consisting of 10% TOA and 90% kerosene was stripped with a solution containing 250 g/l of NH_4HF_2. The white crystals (20 g) of $(NH_4)_2ZrF_6$ were heated in a stream of argon and the resulting gas passed into a reactor, where it was contacted with metallic aluminium preheated at 660°C for an hour. Then the reactor was cooled. Analysis of the material lying at the bottom of the reactor revealed that metallic zirconium was present at the deep bottom, being covered by the metallic aluminium thereon. The substance at the deep bottom was collected, crushed and analyzed, revealing that it was 7.5 g of Zr.

Example 2

Crystals of $(NH_4)_2HfF_6$ were obtained by a process in which hafnium extracted with 100% MIBK (methyl isobutyl ketone) was stripped with a solution containing 200 g/l of NH_4HF_2. The crystals, in an amount of 20 g, were heated in a stream of argon to vaporize them. Meanwhile, metallic aluminium was heated at 660°C in a stream of argon to vaporize it. Both vapours were introduced into a reactor for reaction. When the reactor had cooled, the material deposited on its wall was analyzed, revealing that the material was 10.8 g of metallic hafnium.

Example 3

Crystals of $(NH_4)_2ZrF_6$ were obtained by a process in which zirconium extracted with a mixed organic solvent consisting of 60% TBP and 40% aromatic hydrocarbon was stripped with an aqueous solution containing 180 g/l of NH_4F. 20 Grams of the crystals were placed together with metallic magnesium at the bottom of a reactor. The temperature of the reactor was then raised rapidly in a stream of argon, and maintained at 800°C for an hour. Then the reactor was cooled. Analysis of the residue found revealed it to be 7.5 g of metallic zirconium.

Example 4

A total of 10 g of white crystals of TiF_4 was converted into a gas by heating at 600°C in a stream of argon, and this gas was blown into a reactor which was filled up with argon gas and contained metallic aluminium in the molten state. When the reactor had cooled, a black reaction product found on the inside wall and at the bottom proved to be 3.8 g of metallic titanium.

Example 5

A mixed organic solvent consisting of 30% of D_2EHPA and 70% of n-paraffin (paraffin hydrocarbon having 2 to 14 carbon atoms) contained extracted Ti ions in a concentration of 15 g/l. Crystals of $(NH_4)_2TiF_6$ were obtained by contacting this solvent with an aqueous solution containing 150 g/l of NH_4HF_2. 20 Grams of the white crystals $(NH_4)_2TiF_6$ were heated to vaporize them in a stream of argon and the vapour passed to a reactor which was preheated and maintained at 1000°C. Meanwhile, aluminium was vaporized by heating in a stream of argon. The two vapours were brought into contact in a separate reactor. When the latter reactor was cooled, analysis of a black reaction product deposited on the inside wall and at the bottom of the reactor revealed that it was 4.8 g of metallic titanium.

Example 6

A mixed organic solvent consisting of 60% of TBP and 40% of isoparaffin (commercially available under the name "Isoparaffin") which extracted and contained

H_2TiF_6 was brought into contact with an aqueous solution containing 200 g/l of KHF_2 to produce crystals of K_2TiF_6. 20 Grams of the crystals were packed together with 50 g of metallic aluminium at the bottom of a reactor. The reactor was filled up with H_2 gas and the temperature was rapidly raised to 1000°C and maintained there for 2 hours. Then the reactor was cooled. All the residue found on the inside wall and at the bottom of the reactor was collected, washed with 5% HCl, and analysed as 4 g of metallic titanium.

Example 7

Gaseous TiF_4, which was produced by heating 20 g of crystalline TiF_4 at a sufficient temperature in a stream of hydrogen, was transferred to a reactor in which metallic magnesium was preheated at 800°C. The reactor was cooled after an hour. Then black powders deposited on the inside wall and at the bottom of the reactor were collected. They amounted to 7.6 g, and were shown to be of metallic titanium by X-ray diffraction analysis.

Example 8

A gaseous material produced by heating 20 g of $(NH_4)_2TiF_6$ crystals in a stream of argon was blown into a reactor in which metallic magnesium was heated at a temperature above 800°C in a stream or argon. The reactor was cooled after an hour. On dismantling the reactor, the powders deposited in its inside were found to amount to 4.8 g. They were shown to be of metallic titanium by X-ray diffraction analysis.

CLAIMS

1. A process for preparing metallic zirconium, hafnium or titanium, which process comprises bringing a fluorine-containing compound of zirconium, hafnium or titanium into contact with heated metallic aluminium or magnesium, to convert the fluorine-containing compound into the corresponding metal.

2. A process according to claim 1 wherein the fluorine-containing compound is $(NH_4)_2ZrF_6$, $(NH_4)_2HfF_6$, $(NH_4)_2TiF_6$, TiF_4, ZrF_4, HfF_4 or K_2TiF_6.

3. A process according to claim 1 or 2 wherein metallic zirconium or hafnium is prepared and the metallic aluminium or magnesium is heated to a temperature above 400°C.

4. A process according to claim 1 or 2 wherein metallic titanium is prepared and the metallic aluminium or magnesium is heated to a temperature above 220°C.

5. A process according to any one of the preceding claims wherein the contact is with heated metallic aluminium.

6. A process according to any one of the preceding claims wherein the fluorine-containing compound is produced by extracting a zirconium, hafnium or titanium compound into a solvent comprising at least one extracting agent selected from the group consisting of (a) alkylphosphoric acids, (b) alkylarylphosphoric acids, (c) alkylamines, (d) neutral phosphoric acid esters and (e) ketones, and bringing the solution into contact with an aqueous solution containing at least one of F^-, NH_4^+ and K^+ to extract into the aqueous phase zirconium, hafnium or titanium in the form of a fluorine-containing compound thereof.

7. A process according to claim 6 wherein the solvent comprises the extracting agent diluted with petroleum hydrocarbon.

8. A process according to claim 7 wherein metallic zirconium or hafnium is prepared and the aqueous solution contains NH_4^+.

9. A process according to claim 4 wherein the fluorine-containing compound of titanium is produced by extracting a titanium compound into a solvent comprising (1) at least one extracting agent selected from the group consisting of (A) alkylphosphoric acids, (B) alkylarylphosphoric acids, (C) carboxylic acids, (D) oximes and (E) neutral phosphoric acid esters, and (2) petroleum hydrocarbon as diluent, and bringing the solution into contact with an aqueous solution containing at least one of F^-, NH_4^+ and K^+ to extract into the aqueous phase titanium in the form of a fluorine-containing compound thereof.

10. A process according to any one of claims 6-9 wherein the aluminium fluoride or magnesium fluoride produced is treated to recover the fluoride content and this is recycled for use in the aqueous solution.

Fig.1

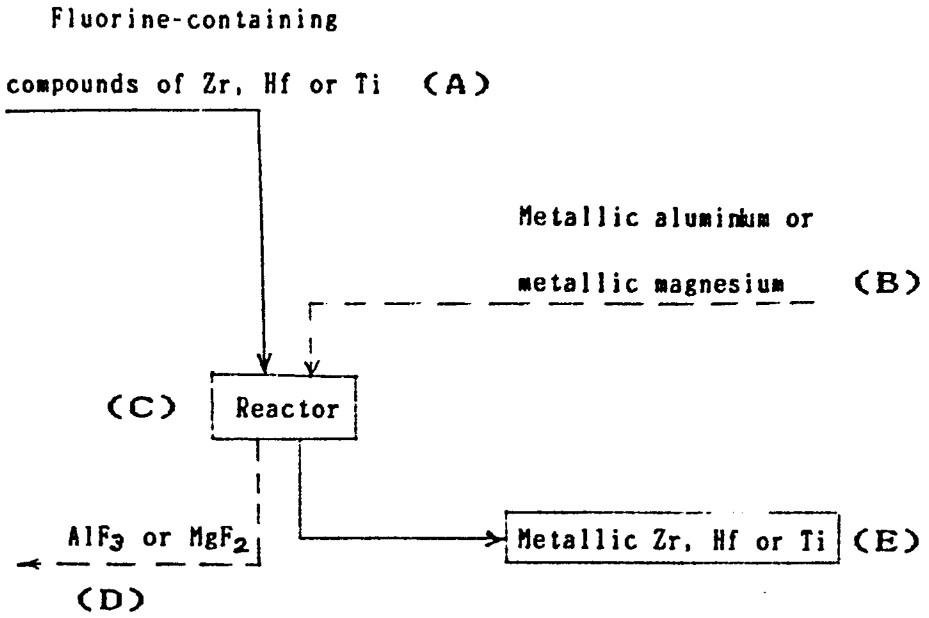

Fluorine-containing compounds of Zr, Hf or Ti (A)
Metallic aluminium or metallic magnesium (B)
(C)
Reactor
AlF$_3$ or MgF$_2$
(D)
Metallic Zr, Hf or Ti
(E)

Fig.2

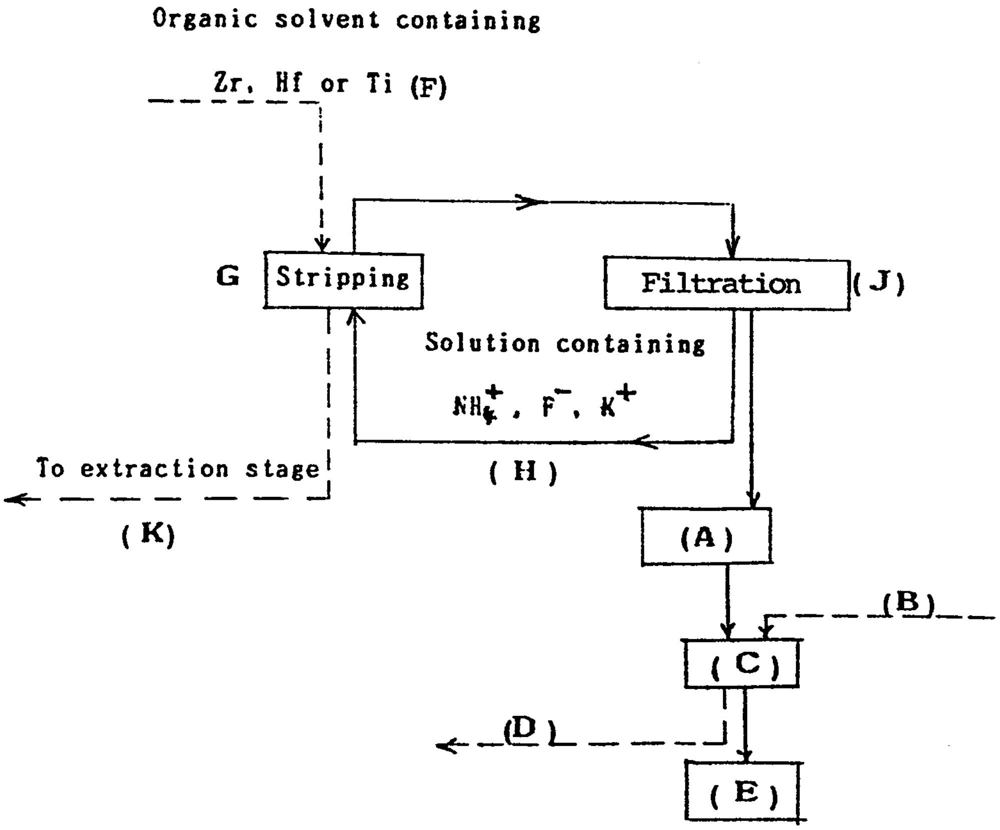
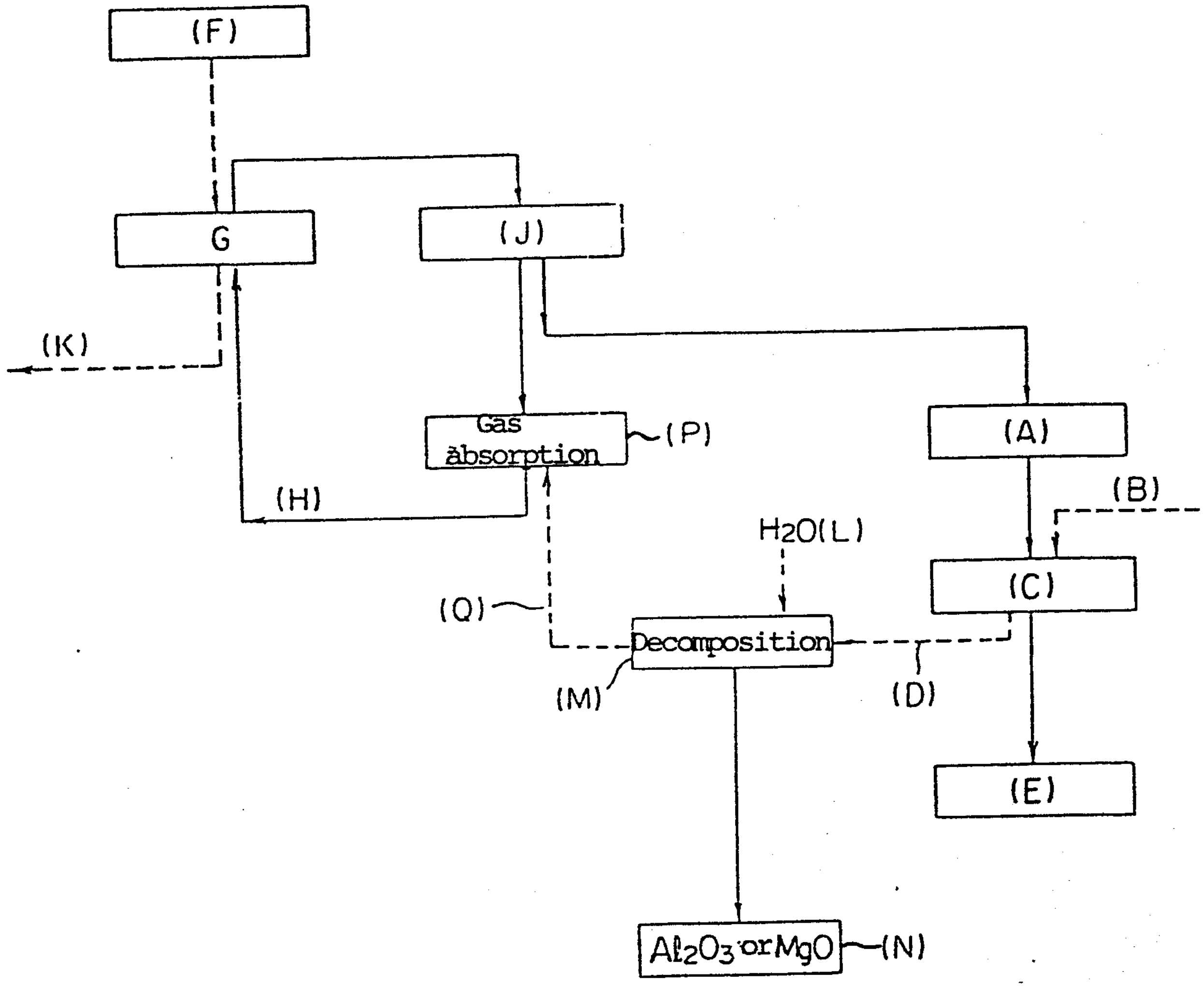

Organic solvent containing Zr, Hf or Ti (F)
G
Stripping
Filtration
(J)
Solution containing NH$_4^+$, F$^-$, K$^+$
(H)
To extraction stage
(K)
(A)
(B)
(C)
(D)
(E)

FIG. 3


(F)
G
(J)
(K)
Gas absorption
(P)
(A)
(H)
(B)
H2O(L)
(C)
(Q)
Decomposition
(M)
(D)
(E)
Al2O3 or MgO
(N)