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(54) Process for producing metallic niobium or metallic tantalum.

(57) Metallic niobium or metallic tantalum is produced by a process which comprises bringing a fluorine containing compound of niobium or tantalum:

(A) into contact with a gas comprising hydrogen at a temperature of at least 400°C; or

(B) into contact with metallic aluminium, metallic magnesium or metallic lead, at a temperature of at least 300°C;

to convert the fluorine containing compound into the corresponding metal.

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PROCESS FOR PRODUCING METALLIC NIOBIUM OR METALLIC TANTALUM

The present invention relates to a process for producing metallic niobium or metallic tantalum.

Conventional processes for producing metallic niobium (Nb) or metallic tantalum (Ta) include reducing their chlorides with metallic magnesium or metallic sodium; using the aluminium Thermit process; and molten salt electrolysis. These conventional processes are complex and the use of metallic magnesium or metallic sodium is costly.

The present invention provides a new, improved, process. In this process, a fluorine containing compound of niobium or tantalum is reacted with hydrogen gas, metallic magnesium, metallic aluminium or metallic lead, to produce metallic niobium or metallic tantalum.

Accordingly, the invention provides a process for producing metallic niobium or metallic tantalum, which process comprises bringing a fluorine containing compound of niobium or tantalum:

(A) into contact with a gas comprising hydrogen at a temperature of at least 400°C; or

(B) into contact with metallic aluminium, metallic magnesium or metallic lead, at a temperature of at least 300°C;

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 in (B) can be conducted in the presence of an inert gas or a reducing gas. Alternatively in (B), 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, magnesium or lead.

Preferably, the fluorine containing compound in the present reaction is gaseous. The compound may contact initially as a solid with the aluminium, magnesium or lead and then be heated to make it gaseous. In a preferred embodiment, in (B) the reaction is conducted with the compound being gaseous and being in an inert gas or a reducing gas.

Thus, the present reaction is preferably between gaseous NbF_5 or gaseous TaF_5 and the hydrogen, aluminium, magnesium or lead, the gaseous NbF_5 or gaseous TaF_5 being comprised in the gaseous fluorine containing compound of niobium or tantalum. The gaseous NbF_5 or gaseous TaF_5 in (B) is preferably employed in the inert gas or reducing gas mentioned above.

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

The fluorine containing compound of niobium or tantalum can be produced by extracting a niobium or tantalum compound into an organic solvent, and bringing the solution into contact with an aqueous solution containing NH_4^+ (and preferably also F^-) to extract into the aqueous phase niobium or tantalum in the form of a fluorine containing compound of niobium or tantalum. 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 embodiment, the organic solvent comprises at least one extracting agent (for example one or two) selected from the group

consisting of (a) alkylphosphoric acids, (b) neutral phosphoric esters, (c) alkylamines and (d) ketones. Preferably, the organic solvent comprises (i) at least one extracting agent selected from (a), (b), (c) and (d), and (ii) a diluent which is a petroleum hydrocarbon.

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

Fig. 1 is a flow sheet illustrating the production using hydrogen gas as reducing agent;

Fig. 2 is a flow sheet illustrating the production using as reducing agent metallic Al, metallic Mg or metallic Pb;

Fig. 3 is a flow sheet illustrating the production of metallic Nb or metallic Ta including the preparation of fluorine containing compounds of Nb or Ta; and

Fig. 4 is a flow sheet similar to Fig. 3 containing a stage for treating by-product gases produced in the reaction stage.

Referring to the drawings, Fig. 1 illustrates the production of Nb or Ta. Fluorine containing compounds (A) of Nb or Ta are supplied to the vaporization stage (B) to produce gaseous NbF_5 or TaF_5. The gaseous NbF_5 or TaF_5 is transferred to a reactor which is full of hydrogen gas (C) and the temperature is maintained at above 400°C (Reaction stage (D)). In this stage, metallic Nb or metallic Ta can be produced according to the following equations:

$$NbF_5 + 2.5H_2 \longrightarrow Nb + 5HF \qquad (1)$$

$$TaF_5 + 2.5H_2 \longrightarrow Ta + 5HF \qquad (2)$$

Fig. 2 illustrates the production using as

reducing agent metallic aluminium, metallic magnesium or metallic lead, instead of hydrogen gas. Gaseous TaF_5 or NbF_5 is prepared by supplying fluorine containing compounds of Ta or Nb (A), such as crystals of $(NH_4)_2TaF_7$ or $(NH_4)_2NbF_7$, respectively, to the vaporization stage (B) and heating them at a temperature above 150°C, as expressed by the following equations:

$$(NH_4)_2NbF_7 \rightleftarrows 2NH_4F\uparrow + NbF_5\uparrow \quad (3)$$

$$(NH_4)_2TaF_7 \rightleftarrows 2NH_4F\uparrow + TaF_5\uparrow \quad (4)$$

In the reaction stage (D), an inert gas or a reducing gas fills the reactor and metallic aluminium, metallic magnesium or metallic lead heated to above 300°C is supplied to the reactor. The NbF_5 or TaF_5 supplied from the vaporization stage (B) to the reaction stage (D) produces metallic Nb or Ta, respectively, by reduction. This reaction stage (D) may be carried out in vacuum.

$$NbF_5 + 1\tfrac{2}{3}\ Al \rightleftarrows Nb\downarrow + 1\tfrac{2}{3}\ AlF_3\uparrow \quad (5)$$

$$TaF_5 + 1\tfrac{2}{3}\ Al \rightleftarrows Ta\downarrow + 1\tfrac{2}{3}\ AlF_3\uparrow \quad (6)$$

$$NbF_5 + 2\tfrac{1}{2}\ Mg \rightleftarrows Nb\downarrow + 2\tfrac{1}{2}\ MgF_2\uparrow \quad (7)$$

$$TaF_5 + 2\tfrac{1}{2}\ Mg \rightleftarrows Ta\downarrow + 2\tfrac{1}{2}\ MgF_2\uparrow \quad (8)$$

$$NbF_5 + 2\tfrac{1}{2}\ Pb \rightleftarrows Nb\downarrow + 2\tfrac{1}{2}\ PbF_2\uparrow \quad (9)$$

$$TaF_5 + 2\tfrac{1}{2}\ Pb \rightleftarrows Ta\downarrow + 2\tfrac{1}{2}\ PbF_2\uparrow \quad (10)$$

Fig. 3 illustrates the process of the invention including the preparation of fluorine containing

compounds (A) of Nb or Ta and also the recovery of HF produced as by-product in the reaction stage.

The organic solution (H) containing extracted Nb or Ta is delivered to the stripping stage (J) and allowed to contact with the aqueous solution (K) containing F^- and NH_4^+. The Nb or Ta is transferred to the aqueous phase, and the organic solvent (P) is transferred to the circulation route to the extraction stage. The transfer can be expressed by the following equations:

$$H_2NbF_7.nTBP + 2NH_4F \rightleftharpoons nTBP + (NH_4)_2NbF_7 + 2HF \quad (11)$$

$$H_2TaF_7.nTBP + 2NH_4HF_2 \rightleftharpoons nTBP + (NH_4)_2TaF_7 + 2HF \quad (12)$$

$$R_5Nb + 5NH_4HF_2 \rightleftharpoons 5RH + (NH_4)_2NbF_7 + 3NH_4F \quad (13)$$

$$R_5Ta + 5NH_4HF_2 \rightleftharpoons 5RH + (NH_4)_2TaF_7 + 3NH_4F \quad (14)$$

$$(R_3NH^+)_2.NbF_7^{2-} + 2NH_4HF_2 \rightleftharpoons 2R_3NH^+.F^- + (NH_4)_2NbF_7 + 2HF \quad (15)$$

$$(R_3NH^+)_2.TaF_7^{2-} + 2NH_4HF_2 \rightleftharpoons 2R_3NH.F^- + (NH_4)_2TaF_7 + 2HF \quad (16)$$

In these equations, TBP represents tributyl phosphate and R is such that RH represents an extracting agent having an H-type exchanging group. It should be understood that the chemical species of the niobium or tantalum compound crystal obtained varies according to the molar ratio NH_4^+/F^- in the solution containing both NH_4^+ and F^- as well as the species appearing in the equations above.

The crystals formed are separated by filtration in the separation stage (L), and the subsequent operations to obtain metallic Nb or Ta are as shown in Fig.1. The by-product HF gas (F) in the reaction stage (D) is absorbed for recovery in the gas absorbing stage (M) where a solution containing NH_4^+ and F^- circulates.

The process illustrated in Fig.4 is basically the

same as that in Fig. 3, but differs in that as reducing agent (C) there is used metallic aluminium, metallic magnesium or metallic lead, and by-product gases produced in the reaction stage (D) are AlF_3, MgF_2 or PbF_2 as illustrated in equations (5) to (10) above.

The gases (F), AlF_3, MgF_2 or PbF_2, produced as by-product in the reaction stage (D) react with H_2O or moist air supplied in the oxidation stage (N) and are converted into easily recoverable HF gas, as expressed by the following equations:

$$2AlF_3 + 3H_2O \rightleftharpoons Al_2O_3 + 6HF \quad (17)$$

$$MgF_2 + H_2O \rightleftharpoons MgO + 2HF \quad (18)$$

$$PbF_2 + H_2O \rightleftharpoons PbO + 2HF \quad (19)$$

The oxides produced, Al_2O_3, MgO or PbO, contain as little fluorine as is permissible for commercial material. The HF gas is recovered in the gas absorbing stage (M).

It is an advantage of the present invention that the fluoride content of the by-product produced in the present basic reaction, i.e. of the HF, AlF_3, MgF_2 or PbF_2, can be recovered and recycled for use in the aqueous solution discussed above which is preferably employed to produce the fluorine containing compound of niobium or tantalum.

In the present invention, gaseous TaF_5 or NbF_5 can be produced by vaporization of fluorine containing compounds of Nb or Ta such as $(NH_4)_2NbF_7$ or

$(NH_4)_2TaF_7$. The vaporization can be carried out using an external heating furnace, an external heating type rotary furnace or naturally a flow type external heating furnace.

The gaseous NbF_5 or gaseous TaF_5 is preferably prepared by heating $(NH_4)_2NbF_7$ or $(NH_4)_2TaF_7$ at a temperature above 150°C.

For the reactor used in the invention, furnaces of various known types can be employed such as the closed type of electric furnace, shaft furnace, rotary or static type of external heating furnace. Metallic aluminium, magnesium or lead used as

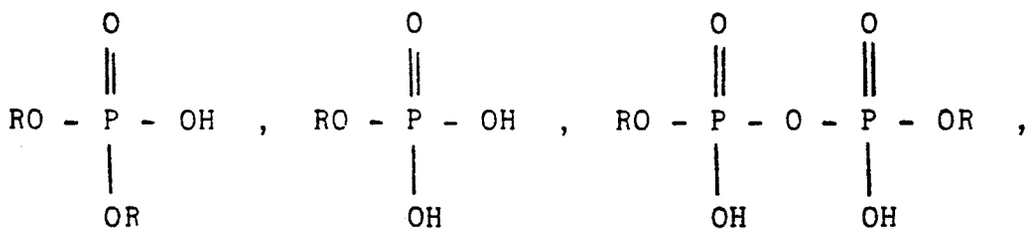
reducing agent may be employed in the form of a gas or liquid or mixture thereof.

The metallic Nb or Ta can be produced by bringing the gaseous fluoride in a stream of an inert gas or a reducing gas or in vacuum into contact with the metallic reducing agent.

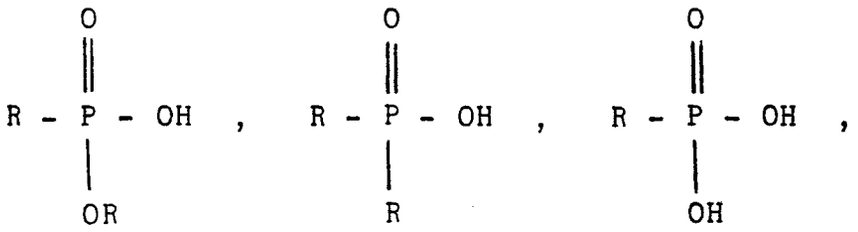
The inert gas which can be employed to maintain the reaction condition of the reactor can be selected for example from the group consisting of argon, helium and nitrogen. Reducing gases which can be employed in the invention include H_2, CO and various gaseous hydrocarbons C_mH_n.

The alkylphosphoric acids which can be employed as extracting agents in the invention, to produce fluorine containing compounds of Nb or Ta, are selected from the group consisting of the following compounds:

(a) (b) (c)



(d) (e) (f)

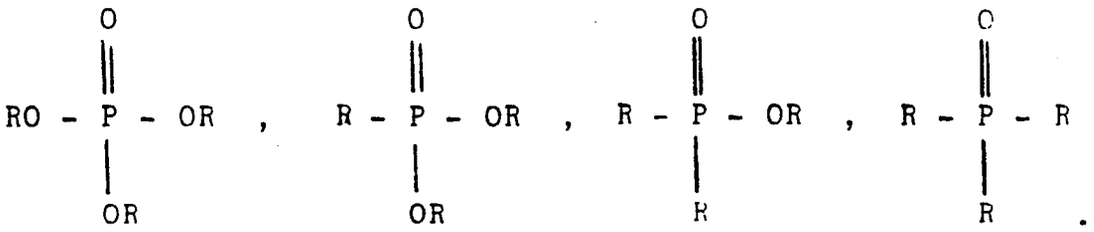


where R represents an alkyl group, generally of 4 to 22 carbon atoms.

The neutral phosphoric esters which can be

employed as extracting agents are selected from the following compounds:

(a) (b) (c) (d)



R is as defined above. TBP (tributyl phosphate) used in the Examples and referred to above is of formula (a) where R = C_4H_9.

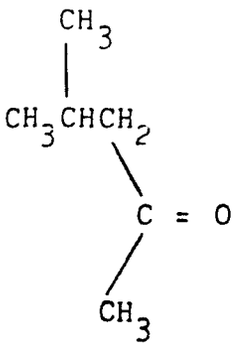
The alkylamines which can be employed as extracting agents are selected from the following group of compounds:

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.

An example of a ketone which can be employed as extracting agent is as follows:



In addition to the above-mentioned compounds, cyclohexanone ($C_6H_{12}O$) is also often employed.

The diluents which can be employed are mostly petroleum hydrocarbons, but aromatic and aliphatic hydrocarbons and mixtures thereof may also be used. For example, kerosene, a mixture of many kinds of hydrocarbon, is commonly used.

The concentration of extracting agent should be chosen according to the character of the treated solution, the concentration of metal ions, the concentration and nature of impurities, and the nature of the chemical species to be extracted, but generally is 2 to 100% by volume.

The invention is illustrated by the following Examples, which describe preferred embodiments:

Example 1:

H_2TaF_7 extracted by a solvent consisting of 60% by volume TBP and 40% by volume aromatic (the aromatic being Shellsol AB), was stripped by an aqueous solution containing 250 g/l of NH_4F, to obtain crystals of $(NH_4)_2TaF_7$. 20 g of these crystals were introduced into a vaporization furnace and heated to 220°C under a stream of H_2 gas. Gaseous TaF_5 formed in the vaporization furnace and was transferred to a reactor which was maintained at a temperature of 600°C. The reaction was continued for an hour, and then the reactor was cooled. A substance had adhered to the inner wall of the reactor, and this substance proved to be Ta, as confirmed by X-ray diffraction analysis. The substance amounted to10 g.

Example 2:

H_2NbF_7 extracted by 100% MIBK (methyl isobutyl ketone) was stripped with an aqueous solution containing 250 g/l of NH_4HF_2, to obtain crystals of $(NH_4)_2NbF_7$, of which 180 g was heated in an atmosphere of helium to produce NbF_5. The NbF_5 gas was continuously treated in a reactor in which the NbF_5 containing gas just obtained was blown onto an aluminium metal surface heated at 950°C in a helium stream. After 6 hours of continuous treatment, the reactor was cooled and disassembled. A substance was found on the aluminium surface in an amount of 62 g and this substance proved to be metallic Nb, as confirmed by X-ray diffraction analysis and chemical analysis.

Example 3:

H_2NbF_5 extracted by a solvent consisting of 80% by volume cyclohexanone and 20% by volume Shellsol AB was stripped with an aqueous solution containing 200 g/l of NH_4HF_2, to obtain crystals of $(NH_4)_2NbF_7$. These crystals and metallic lead were heated separately in an external heating furnace. Gases of metallic Pb and NbF_5 were led to a reactor and held for 2 hours at a

reactor temperature of 750°C. The reactor was then cooled and disassembled. Powder adhering to the inner wall of the reactor proved to be metallic Nb by X-ray diffraction measurement and chemical analysis.

CLAIMS

1. A process for producing metallic niobium or metallic tantalum, which process comprises bringing a fluorine containing compound of niobium or tantalum:

(A) into contact with a gas comprising hydrogen at a temperature of at least 400°C; or

(B) into contact with metallic aluminium, metallic magnesium or metallic lead, at a temperature of at least 300°C;

to convert the fluorine containing compound into the corresponding metal.

2. A process for producing metallic niobium or metallic tantalum, which process comprises bringing gaseous NbF_5 or gaseous TaF_5 into contact with a gas comprising hydrogen at a temperature of at least 400°C, to convert the NbF_5 or TaF_5 into the corresponding metal.

3. A process for producing metallic niobium or metallic tantalum, which process comprises bringing gaseous NbF_5 or gaseous TaF_5 into contact with metallic aluminium, metallic magnesium or metallic lead, at a temperature of at least 300°C, to convert the NbF_5 or TaF_5 into the corresponding metal.

4. A process according to claim 3 wherein the gaseous NbF_5 or gaseous TaF_5 is in an inert gas or a reducing gas.

5. A process according to claim 1 wherein the fluorine containing compound of niobium or tantalum is prepared by extracting a niobium or tantalum compound into an organic solvent comprising at least one extracting agent selected from the group consisting of (a) alkylphosphoric acids, (b) neutral phosphoric esters, (c) alkylamines and (d) ketones, and bringing the solution into contact with an aqueous solution containing NH_4^+ to extract into the aqueous phase niobium or tantalum in the form of a fluorine containing compound of niobium or tantalum.

6. A process according to any one of claims 2-4 wherein the gaseous NbF_5 or gaseous TaF_5 is prepared by heating a fluorine containing compound of niobium or tantalum, which compound has been produced by extracting a niobium or tantalum compound into an organic solvent comprising (i) at least one extracting agent selected from the group consisting of (a) alkylphosphoric acids, (b) neutral phosphoric esters, (c) alkylamines and (d) ketones, and (ii) a diluent which is a petroleum hydrocarbon. and bringing the solution into contact with an aqueous solution containing NH_4^+ to extract into the aqueous phase niobium or tantalum in the form of a fluorine containing compound of niobium or tantalum.

7. A process according to any one of claims 2-4 and 6 wherein the gaseous NbF_5 or gaseous TaF_5 is prepared by heating $(NH_4)_2NbF_7$ or $(NH_4)_2TaF_7$ at a temperature above 150°C.

8. A process according to any one of claims 2-4 wherein the gaseous NbF_5 or gaseous TaF_5 is prepared by heating a fluorine containing compound of niobium or tantalum, which compound is prepared as defined in claim 5.

9. A process according to any one of the preceding claims wherein metallic tantalum is produced by a process comprising bringing gaseous TaF_5 into contact with a gas comprising hydrogen at a temperature of at least 400°C, to convert the TaF_5 into metallic tantalum.

10. A process according to any one of claims 1-8 wherein metallic niobium is produced by a process comprising bringing gaseous NbF_5:

(a) in helium into contact with metallic aluminium; or

(b) into contact with gaseous metallic lead;

at a temperature of at least 300°C, to convert the NbF_5 into metallic niobium.

FIG.1

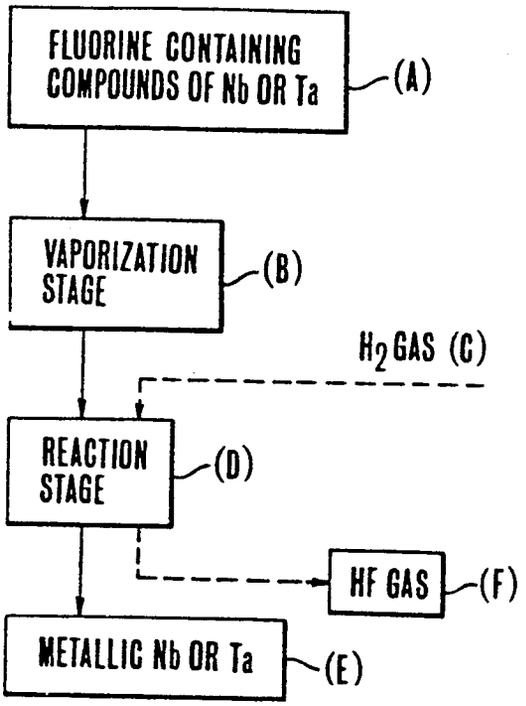
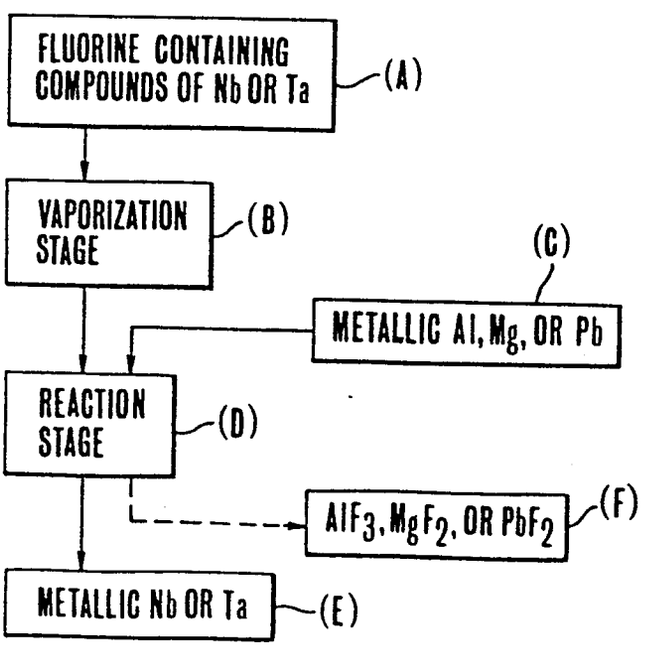

FLUORINE CONTAINING COMPOUNDS OF Nb OR Ta
(A)
VAPORIZATION STAGE
(B)
H_2 GAS (C)
REACTION STAGE
(D)
HF GAS
(F)
METALLIC Nb OR Ta
(E)

FIG.2


FLUORINE CONTAINING COMPOUNDS OF Nb OR Ta
(A)
VAPORIZATION STAGE
(B)
(C)
METALLIC Al, Mg, OR Pb
REACTION STAGE
(D)
AlF_3, MgF_2, OR PbF_2
(F)
METALLIC Nb OR Ta
(E)

2/2

FIG.3

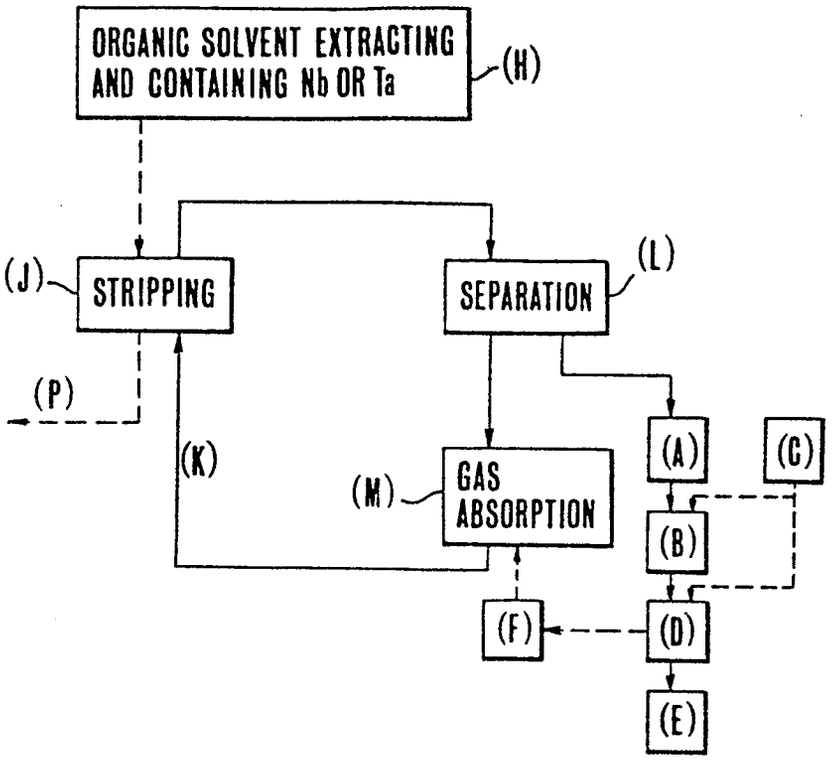
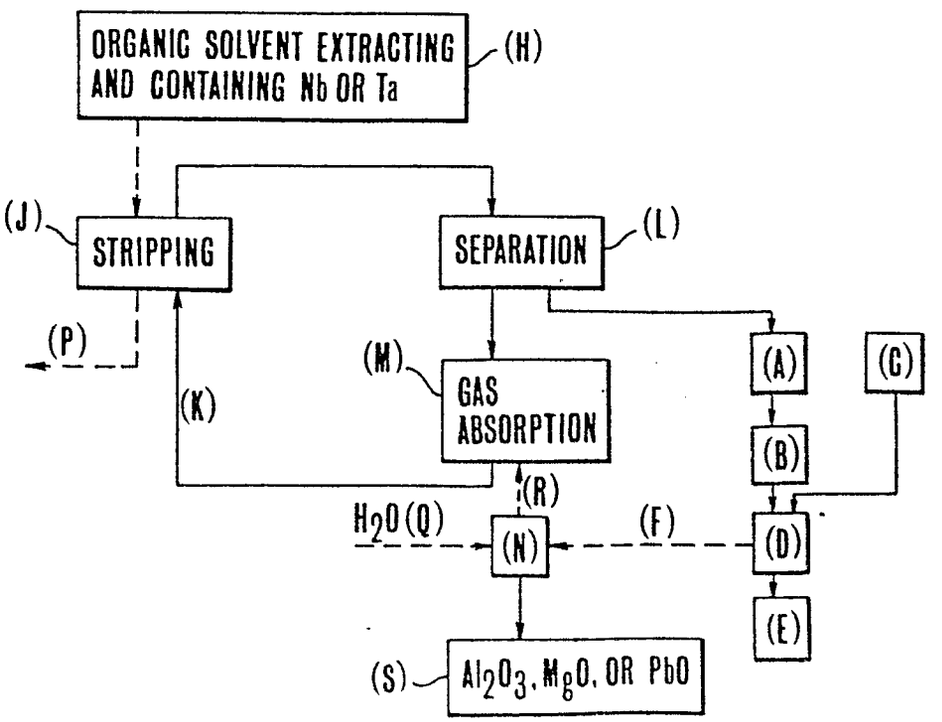

ORGANIC SOLVENT EXTRACTING AND CONTAINING Nb OR Ta
(H)
(J)
STRIPPING
SEPARATION
(L)
(P)
(K)
(M)
GAS ABSORPTION
(A)
(C)
(B)
(F)
(D)
(E)

FIG.4


ORGANIC SOLVENT EXTRACTING AND CONTAINING Nb OR Ta
(H)
(J)
STRIPPING
SEPARATION
(L)
(P)
(K)
(M)
GAS ABSORPTION
(A)
(C)
(B)
(R)
H2O(Q)
(N)
(F)
(D)
(E)
(S)
Al2O3, MgO, OR PbO