



(22) Date de dépôt/Filing Date: 1993/03/03
(41) Mise à la disp. pub./Open to Public Insp.: 1993/09/07
(45) Date de délivrance/Issue Date: 2004/09/21
(30) Priorité/Priority: 1992/03/06 (P 42 07 145.3-24) DE

(51) Cl.Int.⁵/Int.Cl.⁵ C22B 34/24
(72) Inventeurs/Inventors:
ECKERT, JOACHIM, DE;
BLUDBUS, WALTER, DE
(73) Propriétaire/Owner:
H.C. STARCK GMBH & CO. KG, DE
(74) Agent: FETHERSTONHAUGH & CO.

(54) Titre : PROCEDE POUR L'EXTRACTION DU TANTALE ET DU NIOBIUM
(54) Title: PROCESS FOR ISOLATING TANTALUM AND NIOBIUM

(57) **Abrégé/Abstract:**

The present invention relates to a hydrometallurgical process for isolating tantalum and niobium from raw materials containing tantalum and niobium by treatment with pure hydrofluoric acid or a mixture of hydrofluoric acid and sulphuric acid, followed by solvent extraction of the tantalum and niobium fluoro-complexes from the treatment solution using methylisobutyl ketone (MIBK) and steam distillation of the organic ketone phase containing tantalum and niobium, to produce a new aqueous which is contactable by fresh MIBK to selectively extract tantalum.



A process for isolating tantalum and niobium**Abstract of the Disclosure**

The present invention relates to a hydrometallurgical process for isolating tantalum and niobium from raw materials containing tantalum and niobium by treatment with pure hydrofluoric acid or a mixture of hydrofluoric acid and sulphuric acid, followed by solvent extraction of the tantalum and niobium fluoro-complexes from the treatment solution using methylisobutyl ketone (MIBK) and steam distillation of the organic ketone phase containing tantalum and niobium, to produce a new aqueous which is contactable by fresh MIBK to selectively extract tantalum.

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5 A process for isolating tantalum and niobium**Field and Background of the Invention**

10 The present invention relates to a hydrometallurgical process for isolating tantalum and niobium from raw materials which contain tantalum and niobium by treatment with pure hydrofluoric acid or a mixture of hydrofluoric acid and sulphuric acid, followed by solvent extraction of the tantalum and niobium complexes from the treatment solution using methylisobutyl ketone and steam distillation of the organic ketone phase containing tantalum and niobium.

15 Tantalum and niobium occur together in most natural sources. Different proportions of the two elements, however, characterise the ores and their geological deposits. Niobium is in principle obtained from columbite ore and/or pyrochlore ore from Brazil and Canada and other regions. These ores, however contain only small amounts of tantalum. Tantalum-rich ores, such as e.g. tantalite, contain correspondingly small amounts of
20 niobium.

To isolate tantalum and niobium, however, it is mainly slags which are produced during the isolation of tin (Thailand, Brazil) which are also used. These tin slags are now regarded as the most important raw material source for the two elements, although they
25 only contain small amounts of niobium and tantalum. Also, very variable Ta/Nb ratios are encountered in these tin slags.

Normally, the two metals and their compounds are isolated indirectly from raw materials containing very little tantalum and niobium, such as e.g. tin slags, by fusion metallurgical enrichment methods for the two elements. Only the synthetic tantalum/niobium
30 concentrates obtained in this way are available for economic wet chemical processing. Among these tin slags there are now also those which, like natural columbite, contain tantalum in a very unfavourable Ta/Nb ratio, i.e. they contain small amounts of tantalum but are rich in niobium. The normal hydrometallurgical treatment and separation processes cannot be applied to these, for economic reasons, because these processes
35 require a Ta/Nb ratio of at least 1:3 in the concentrate which is used.

5 The conventional hydrometallurgical process for isolating tantalum or niobium, disclosed
in US Patent 3,117,833, comprises treatment of the tantalum/niobium raw material in
mineral acids, preferably hydrofluoric/sulphuric acid mixtures. Tantalum and niobium are
thereby dissolved together as fluoro-complexes and subsequently separated first from
10 accompanying elements and then from each other, using a multi-stage solvent extraction
with MIBK (methylisobutyl ketone, 2-methyl-pentan -4- one). Here, the fluoroniobates or
fluorotantalates are selectively re-extracted in sequence and further processed to give
pure tantalum or niobium compounds.

15 In detail, this takes place by selectively removing the niobium from the organic ketone
phase which contains niobium and tantalum, e.g. with dilute sulphuric acid, while
tantalum remaining in the organic phase may be re-extracted from that using water.

20 However, if materials which are rich in niobium but contain very little tantalum are used,
then at this point the tantalum is present in very low concentration in the organic ketone
phase. This means that there is a very poor volume/time yield, which makes the process
uneconomical.

25 In addition, US Patent 3,403,983 discloses a process for the preparation of an aqueous
solution of niobium and/or tantalum fluoro-complexes from a solution of fluoro-
complexes of these metals in a steam-volatile, organic solvent which is virtually
immiscible with water, wherein a solution of the fluoro-complexes of these metals in the
organic solvent, which is obtained using the known multi-stage extraction of the metals
from ores, is subjected to a steam distillation process with quantitative evaporation of the
solvent to produce a non-distilled aqueous solution which contains the fluoro-complexes
in a higher concentration than was present in the organic solvent.

30 This should mean that the problem of emulsion formation is avoided, the organic solvents
are easily recovered and recycled, an aqueous solution of niobium and/or tantalum fluoro-
complexes with three- to four-fold higher concentrations than in solution in the organic
solvent is obtained and the aqueous product solution is highly suitable for the economic
35 crystallisation of K_2TaF_7 .

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This does not apply in particular, therefore, to niobium/tantalum complexes which contain very little tantalum.

Therefore, there is a need for a process for economically isolating tantalum from starting materials which contain very little tantalum and at the same time are rich in niobium, using a wet chemical treatment and extraction process, without an indirect fusion metallurgical process being required beforehand. In addition, all the niobium should also be isolated.

Summary

According to the invention, the raw material containing tantalum and niobium, e.g. tin slags, niobium ores and/or concentrates, is treated with pure hydrofluoric acid or a mixture of hydrofluoric acid and sulphuric acid and the acid solution is extracted first with MIBK (methylisobutyl ketone), wherein niobium and tantalum pass into the organic phase together. Normally, the sum of the transition metals, calculated as their oxides, is expressed as "combined oxides" (abbrev.: "C.O."). The niobium is not now selectively re-extracted from the organic phase using mineral acids or water, as is usual, but the ketone phase containing the C.O. is subjected to steam distillation. This measure means that both valuable substances are converted into an aqueous phase in a highly concentrated form. The tantalum is now selectively extracted from this aqueous phase using fresh ketone (MIBK), while the niobium remains in the aqueous phase.

This invention thus comprises a hydrometallurgical process for isolating tantalum and niobium from raw materials containing tantalum and niobium by treatment with pure hydrofluoric acid or a mixture of hydrofluoric acid and

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sulphuric acid, followed by solvent extraction of the tantalum and niobium fluoro-complexes from the treatment solution using methylisobutyl ketone and steam distillation of the organic ketone phase containing tantalum and niobium, 5 wherein the tantalum is selectively extracted from the newly produced aqueous phase with fresh methylisobutyl ketone, while all the niobium remains in the aqueous phase.

5 By selecting the ratio between the organic and aqueous phases, the amount of tantalum in
the new MIBK phase may be adjusted to the desired concentration. If this organic phase
is subjected to a further steam distillation process, there is another increase in the
concentration of tantalum in the new aqueous phase. A preferred embodiment of the
process according to the invention comprises treating the new organic ketone phase
10 containing tantalum with steam and thereby re-extracting the tantalum. The new
concentrated tantalum solution may then be further processed in known ways.

The process according to the invention is advantageously useable for various
tantalum/niobium raw materials. It confers particular advantages if there is a Ta:Nb ratio
of ≤ 0.2 in the raw materials containing tantalum and niobium. Preferably, the process may
15 be applied to columbite ores and/or tin slags with a Ta:Nb ratio of 1:5 to 1:15.

Detailed Description of Preferred Embodiments

The invention is explained in more detail in the following by way of example, without this
20 being regarded as a limitation.

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5 Example

A columbite ore with 35% by weight of Nb_2O_5 and 4% by weight of Ta_2O_5 , the remainder being SiO_2 , FeO , MnO_2 , TiO_2 and other impurities, was treated with 70% strength pure hydrofluoric acid. This produced a solution with 135 g/l of C.O. (= Combined Oxides, Nb_2O_5 and Ta_2O_5) and an acidity of 20 N. The Ta:Nb ratio in this starting solution was about 1:9, corresponding to the starting material. This feed solution was passed against an organic phase consisting of methylisobutyl ketone (MIBK) in a counter-stream solvent extraction unit. The raffinate was sufficiently free of valuable material, with 0.3 g/l of C.O. The ketone phase containing 89 g/l of C.O. was now washed with a little 12 normal sulphuric acid, in order to remove residual impurities of other elements which had also been extracted. The ketone phase containing niobium and tantalum was sluiced out and subjected to steam distillation. 130 l/h TaNb MIBK were continuously fed to the top of a distillation column whereas 50 l/h steam were fed to the bottom of this column. The MIBK was totally distilled off and 35-40 l/h of a concentrated Niobium- und Tantalum solution remained behind. These elements were present as fluoro-complexes in a concentration ratio of 20 g/l Ta_2O_5 and 180 g/l Nb_2O_5 (Ta:Nb = 1:9). Due to the relatively low acidity of the aqueous phase of this steam distillation process the tantalum now was selectively extracted by contacting 40 l/h of this aqueous solution with 5 l/h of fresh unloaded MIBK while the niobium (180 g/l Nb_2O_5) remained in the aqueous phase and was worked up separately. The resulting organic phase containing tantalum (with 140 g/l Ta_2O_5) was again treated with steam (3 l Ta MIBK / 1 l steam) which totally removed the MIBK from the system and produced the concentrated aqueous solution of tantalum fluorid (with >200 g/l of Ta_2O_5 equivalent). This was converted into the endproduct potassium hepta fluorotantalate (1,4 kg) by the addition of KCl in the usual way as described for example in US Patent 3,051,547.

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5 Comparison example (according to US Patent 3,117,833)

10 The niobium/tantalum solution produced from treatment of the ore used in example 1 was, as in example 1, passed against an organic phase consisting of methylisobutyl ketone (MIBK) in a counter-stream solvent extraction unit. The ketone phase, containing 90 g/l of C.O., was now washed with a little 12 normal sulphuric acid, in order to remove residual impurities of other elements which had also been extracted. The niobium was selectively and completely converted into an aqueous phase, in the usual way, by stripping it from the ketone phase containing niobium and tantalum with 2 N sulphuric acid and this was used as a sulphuric acid niobium fluoride solution to isolate niobium
15 hydroxide. The ketone phase, now only containing tantalum, with 7.5 g/l of Ta₂O₅, was freed of ketone by steam distillation and converted into an aqueous phase containing <25 g/l of Ta₂O₅. This solution, with the relatively low tantalum content, is not suitable for economic further processing since it either requires too much heat energy for evaporation or leaves behind too much salt-laden waste water, if tantalum hydroxide is produced from
20 it.

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CLAIMS:

1. A hydrometallurgical process for isolating tantalum and niobium from a raw material containing tantalum and niobium by an aqueous treatment solution comprising pure
5 hydrofluoric acid or a mixture of hydrofluoric acid and sulphuric acid, followed by: (a) solvent extraction of the resultant tantalum and niobium fluoro-complexes from the aqueous treatment solution using methylisobutyl ketone (MIBK) (b) steam distillation of the MIBK phase which
10 contains tantalum and niobium to produce an aqueous phase, and (c) the tantalum is selectively extracted from aqueous phase thus produced, using fresh MIBK, while all the niobium remains in the aqueous phase.
2. A process according to claim 1, wherein the fresh
15 MIBK phase containing tantalum is treated again with steam and the tantalum is thereby re-extracted.
3. A process according to claim 1 or 2, wherein a Ta/Nb ratio of ≤ 0.2 is present in the raw material which contains tantalum and niobium.
- 20 4. A process according to claim 1 or 2, wherein the raw material is columbite, tin slag or a mixture thereof with a Ta:Nb ratio of from 1:5 to 1:15.
5. A process according to any one of claims 1 to 4, wherein the distilled-off MIBK phase is condensed and reused
25 in steps (a), (c) or both.

FETHERSTONHAUGH & CO.

OTTAWA, CANADA

PATENT AGENTS