Extraction of Niobium, Tantalum and Titanium from Columbite

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Niobium, tantalum and titanium have become of major interest recently as construction materials for the fusion and fast breeder reactors which are expected to be the next sources of atomic energy. The ores which contain these metals are columbite and tantalite. In Southeast Asia, where these ores are found, low and middle grade quality ores are left unexploited, since it is uneconomic to process them. Economic extraction techniques would thus be of considerable importance.

Since these ores are characterized by very great chemical stability, very complicated process have been required to disintegrate them and to isolate their metallic components. However, such methods are unsuitable for the mass-production techniques which future demand will require. It is from this point of view that we have studied the Nitrofluor process, an ore processing method which has a considerable potential for mass-production technology.

NITROFLUOR PROCESS

The Nitrofluor process is a method of extracting useful metallic components from ores by using the chemistry of the nonaqueous solvent that is obtained by adding NO_2 as a complexing agent to anhydrous HF. The use of this solvent was once investigated for its use in reactor fuel reprocessing (Strickland et al., 1964). In this solvent, each component reacts with nitrosyl fluoride (NOF) produced by Eqs. 1 and 2,

$$N_2O_4 + 2HF \rightleftharpoons F(HF)^- + NO^+ + HNO_3 \qquad (1)$$

$$NO^+ + F(HF)^- \rightleftharpoons NOF + HF \qquad (2)$$

to produce fluoride complexes as shown in Eqs. 3 to 7 (Kigoshi et al. 1973), (Kigoshi et al., 1969),

$$Nb_2O_5 + 12NOF = 2NONbF_6 + 5NO + 5NO_2 \qquad (3)$$

$$Ta_2O_5 + 12NOF = 2NOTaF_6 + 5NO + 5NO_2 \qquad (4)$$

$$TiO_2 + 5NOF = NOTiF_5 + 2NO + 2NO_2 \qquad (5)$$

$$FeO + 4NOF = NOFeF_4 + 2NO + NO_2 \qquad (6)$$

and probably

$$MnO + 4NOF = NOMnF_4 + 2NO + NO_2. \qquad (7)$$

Some of these complexes have sublimation properties while others do not. Our study has concerned the separation of each component by using the difference in sublimation properties. The possibility of using the Nitrofluor process on an industrial scale is suggested.

SPECIMEN AND SOLVENTS

Niobium and tantalum ores produced in the Federation of Malaysia were used as specimens. X-ray and chemical analyses of the elemental components of this ore show it to be a columbite-tantalite mineral containing some iron, titanium and manganese, and very small quantities of tin, silicon, uranium, copper and thorium. The chemical composition is shown in Table 1.

A nonaqueous mixture of 20 mol% NO_2–80 mol% HF was used as a solvent. This solvent was prepared by mixing NO_2 and HF through distillation. NO_2 and HF were made and packed in cylinders at Matheson Co., Inc. and Hashimoto Chemical Engineering Co., respectively.

Quantitative analyses of the metal ions were performed by atomic-absorption spectrophotometry using a Hitachi Model 208 atomic-absorption spectrophotometer.

DISINTEGRATION OF THE COLUMBITE

An adequate quantity of the solvent was added to the columbite in a polypropylene vessel and kept at rest at room temperature. After the appointed period, the dissolver solution was separated by centrifuge from the precipitate and the about 1.5% unreacted ore granule. Then the extent of the reaction was measured by chemical analysis. Almost complete reaction was achieved within ten hours. The chemical composition of the precipitate is given in Table 2. As is obvious from this result, the fluoride complexes of niobium, tantalum, iron and manganese concentrated into the precipitate, while the supernatent solution accumulated titanium. When 1.25 times stoichiometry of solvent was used for the disintegration, about 5.10% of the original niobium and 6.3% of the tantalum were lost into the dissolver solution.

SEPARATION OF NIOBIUM AND TANTALUM BY SUBLIMATION

From the results described above, it is clear that large parts of the niobium, tantalum, iron and manganese were distributed in the precipitate as fluoride complexes.

Among these fluoride complexes, as mentioned before, those of

TABLE 1. CHEMICAL COMPOSITION OF ORE

Component	wt.%	Component	wt.%
Nb_2O_5	61.80	CrO_2	0.20
Ta_2O_5	9.58	MgO	0.08
FeO	15.04	SnO_2	0.50
MnO	5.22	SiO_2	—
TiO_2	5.41	U_3O_8	—
CaO	0.11	ThO_2	—
CuO	0.34	Residue	1.32
		Total	99.60

TABLE 2. CHEMICAL COMPOSITION OF PRECIPITATE

Component	Nb	Ta	Ti	Fe	Mn
Wt.%	27.69	4.61	0.55	4.63	1.95

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niobium and tantalum sublimate at 328°C and 374°C, respectively (Kigoshi, 1975), while those of iron and manganese decompose on heating, leaving nonvolatile fluoride (Kigoshi, 1976). Consequently, purification of the fluoride complexes of niobium and tantalum by sublimation was attempted.

The separation method examined involved the selective condensation and the preceeding volatile transfer of the fluoride complexes in a flow of nitrogen. The apparatus is sketched in Figure 1. This apparatus, made of Monel alloy of 1.2 mm thickness, consists of a sublimation section followed by four condensation ones. The temperature of each of these sections was controlled independently by an electric resistance furnace. Nitrogen gas was allowed to flow at a constant rate through the whole system as the carrier gas.

A preliminary test using an artificial sample of pure $NONbF_6$ and $NOTaF_6$ was performed and complete sublimation was achieved within 3 hours.

The results of the sublimation experiment with this artificial sample are shown in Figure 2. The greater part of $NOTaF_6$ was deposited on the higher temperature part of the condenser while $NONbF_6$ occupied the greater part of the lower temperature region. This phenomenon is as expected from the fact that the sublimation point of $NOTaF_6$ is higher than that of $NONbF_6$.

The next separation studies were conducted with an ore the composition of which is given in Table 1. The chemical compositions of the condensates and of the remnant originating with sublimation at 400°C are given in Table 3. The temperatures of the condenser sections where the deposition occurred are also given in Table 3.

As can be seen in these results, the decontamination of niobium and tantalum from titanium, iron and manganese seems to be almost perfect. Other impurities such as chromium, calcium, copper, tin and magnesium behaved similarly because they also produced nonvolatile fluoride under these conditions. Silicon need not enter consideration either because the sublimation point of $(NO)_2SiF_6$ is 80°C.

The amounts of niobium and tantalum that remain in the remnant after sublimation reach near by 30% of the original and they would have an impact on commercial scale economics. Since the amounts of loss depend closely upon the content of iron and manganese in the remnant, these impurities should be eliminated preceeding the sublimation. An effective countermeasure using anhydrous hydrogen fluoride is being attempted and the results will be reported in the near future.

PURIFICATION OF TITANIUM

As previously described, almost all the titanium in the columbite was extracted into the solution on disintegration. Therefore, when this solution was evaporated to dryness, a solid product containing the fluoride complex of titanium was obtained. The chemical composition of this solid product is shown in Table 4.

Since it is known that the fluoride complex of titanium sublimates at 319°C (Kigoshi, 1975), the purification of this compound from the other components by sublimation was tried. The sublimation experiment was performed for two hours at 320°C. The results are shown in Figure 3. No iron and manganese were detected in the condensate. Though the sublimation point of the fluoride complex of titanium is close to those of niobium and tantalum, no niobium and tantalum were detected in the condensate either.

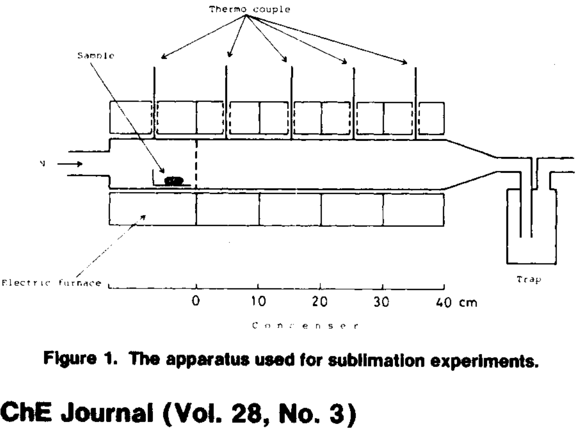

Figure 1. The apparatus used for sublimation experiments.

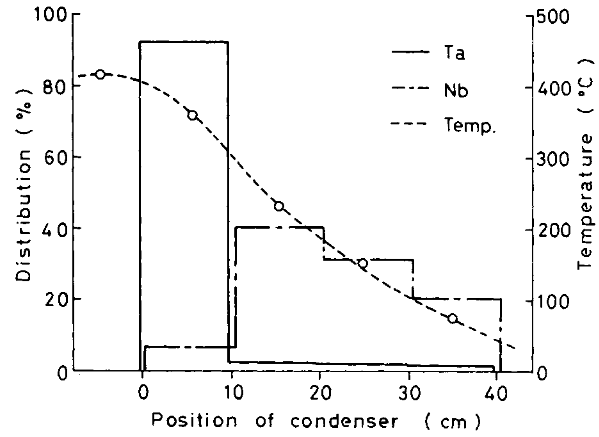

Figure 2. Separation of niobium and tantalum by sublimation with flowing pure nitrogen.

GENERAL ASPECTS

A general conception of the new process which was derived from the present study is summarized in a flowsheet as shown in Figure 4.

When, as in the present case, new processes are proposed, some improvement on present techniques should be aimed at. Thus we have attempted to cost the new process.

As the NO_2-HF solvent can be made at a very low cost, the ores are low-priced and the process can be made very simple, manufacturing costs can be reduced to about one-twentieth of that of present processes. However, it is impossible to arrive at a firm projection, because our proposal would involve not merely a partial improvement of the present process but its total replacement. Consequently, many factors have to be estimated.

As it has been shown that uranium hexafluoride can be recovered from the fluoride complex of uranium by sublimation (Sato, 1979), uranium hexafluoride can be separated, as shown in Figure 4, if the uranium content of the ore is high enough. Thorium oxide does not react with NO_2-HF solvent at all, so it can be recovered in the residue unreacted.

In a continuous commercial scale process, a mutistage sublimator-condenser system would be available. This is based on the fluidized-bed roaster which has been utilized in nonferrous met-

TABLE 3. CHEMICAL COMPOSITION OF SUBLIMATION AND REMNANT FROM COLUMBITE ORE PRECIPITATE

Section	0	1	2	3	4
Temp., °C	400	355	255	105	20
Nb	21.03%	13.26%	93.00%	97.38%	—
Ta	3.50%	86.74%	7.00%	2.62%	—
Ti	1.04%	—	—	—	—
Fe	8.80%	—	—	—	—
Mn	3.71%	—	—	—	—

TABLE 4. CHEMICAL COMPOSITION OF SOLID PRODUCT FROM DRIED SUPERNATENT SOLUTION

Component	Nb	Ta	Ti	Fe	Mn
wt.%	5.61	1.28	7.91	13.78	5.09

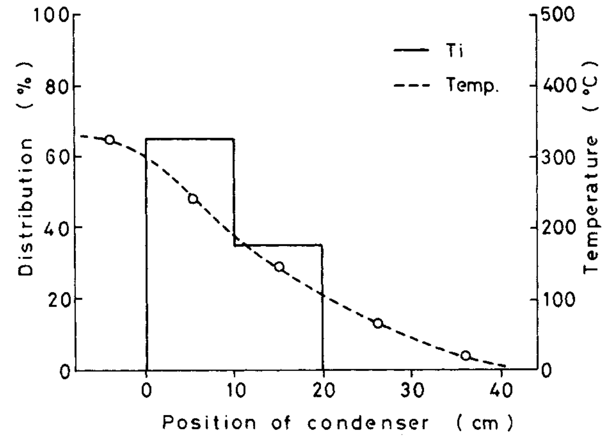

Figure 3. Purification of titanium by sublimation.

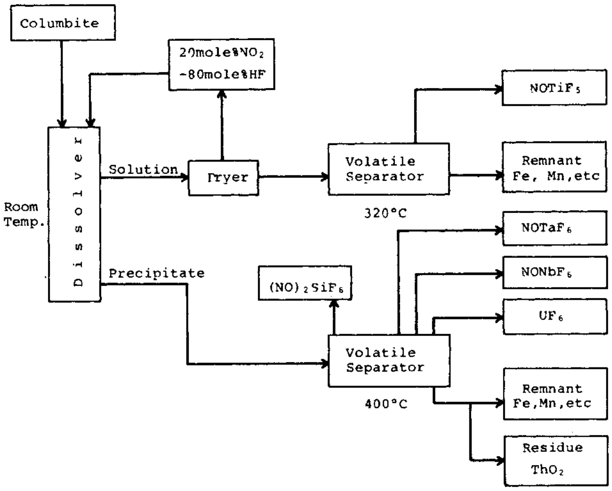

Figure 4. Flowsheet of treating columbite by the Nitrofluor process.

allurgy, and consists of several units installed vertically. A small scale experiment will be started soon.

At the present time, we can say with confidence only that the Nitrofluor process could be expected to out-perform current techniques.

CONCLUSION

In this paper, we have demonstrated the possibility of the extraction of niobium, tantalum and titanium from columbite by the Nitrofluor process. The nonaqueous inorganic solvent consisting of 20 mol% NO_2–80 mol% HF can disintegrate columbite easily, and volatile separation can be achieved at relatively low temperatures.

As, however, the kinetic constants of the solvent, the reaction and the products are not known, further experiments on these are being carried out. Further efforts to improve the separation from both the fundamental and the engineering stand-points are required.

ACKNOWLEDGMENT

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