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The Extraction of Niobium and Tantalum from Columbite by the Nitrofluor Process*

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Synopsis

The Nitrofluor process provides a through method of dissolving the columbite in a nonaqueous inorganic solvent, purifying the niobium and tantalum, and separating them each other by volatile separation techniques.

HF solutions of N_2O_3 , N_2O_4 or NOF can disintegrate the columbite even at a room temperature. Subsequently, most of the niobium and tantalum precipitate as complex fluorides, leaving in the solution relatively large quantities of impurities, such as iron, manganese, titanium and tin.

For further isolation of the complex fluorides of niobium and tantalum from the impurities, a volatilization of the niobium and tantalum from the dissolver solid separated from the dissolver solution is found effective. There appears to be a possibility of separating niobium and tantalum from each other by fractional sublimation utilizing the difference of volatility of these complex fluorides when the HF- N_2O_3 azeotrope is used for disintegrating the columbite.

A general flowsheet for treating typical columbite or tantalite by the Nitrofluor process is proposed.

I. Introduction

Since metals such as beryllium, titanium, zirconium, niobium and tantalum have properties of existing very stable minerals in nature, it requires hard works and complicated processes to disintegrate these ores and to isolate their final metallic component.

The present study was undertaken to obtain some of the fundamental aspects on a process for recovering niobium and tantalum separately from the columbite. The result of experiments shows that the Nitrofluor process⁽¹⁾ provides the possibility.

A disintegration of the columbite was achieved at adequate rates in a nonaqueous HF solution of N_2O_3 , N_2O_4 or NOF even at a room temperature. Subsequently, most of the niobium and tantalum precipitated as complex fluorides leaving relatively large quantities of impurities in the solution. For further isolation of the complex fluoride of niobium and tantalum from the impurities, volatile separation techniques were found to be effective. A niobium-tantalum

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(1) A. Kigoshi, Bull. Japan Inst. Metals, **10** (1971), 734. 42-10 (1972), 73.

separation was expected to be possible by utilizing the difference of volatility of these complex fluorides formed with an HF-N₂O₃ azeotrope used for disintegration of the ore.

Finally, a general flowsheet for recovering niobium and tantalum from typical columbite or tantalite by Nitrofluor process was proposed based on the result of the present experiment.

II. Specimen and solvent

The specimen was niobium and tantalum ore produced in the Federation of Malaysia. Fluorescent X-ray analysis showed that the principal element of the ore is a columbite-tantalite mineral containing some iron and manganese along with a small amount of ilmenite and cassiterite, and very small quantities of yttrium, zirconium, arsenic, uranium and thorium. The chemical composition is shown in Table 1. The residue in Table 1 means remnants which do not react with N₂O₃·12.5 HF in disintegrating the specimen.

Table 1. Chemical composition of ore specimen

Component	wt %	Component	wt %
Nb ₂ O ₅	61.12	SiO ₂	0.48
Ta ₂ O ₅	9.78	ZrO ₂	-
FeO	17.63	ThO ₂	-
MnO	6.56	U ₃ O ₈	-
TiO ₂	2.45	Residue	1.32
SnO ₂	0.40		
		Total	99.76

The solvent which was mainly used in disintegrating the specimen and in purifying the subsequent product is an azeotrope boiling at 68°C.⁽¹⁾ In the present study, this material is produced by the fractional distillation of HF-NO₂ solutions. The 68°C azeotrope is equivalent to N₂O₃·12.5 HF. The materials boiling at 52° and 94°C⁽¹⁾ which were used for reference were produced similarly.

III. Experimental result and consideration

III. 1. Disintegration of ore by the solvent

The particle size of the specimen was from 0.5 to 2 mm as broken into pieces. N₂O₃·12.5 HF was added to the specimen 1.25 times as much as the theoretical quantity, and kept at constant temperature. After the appointed hours, dissolver solution and solid product were separated from unreacted ore granule, and then the extent of reaction was determined by chemical analysis. The results are shown in Fig. 1. Almost complete reaction required was achieved within about 4 or 7 hours at 30°C or 20°C, respectively. There was no significant difference between the

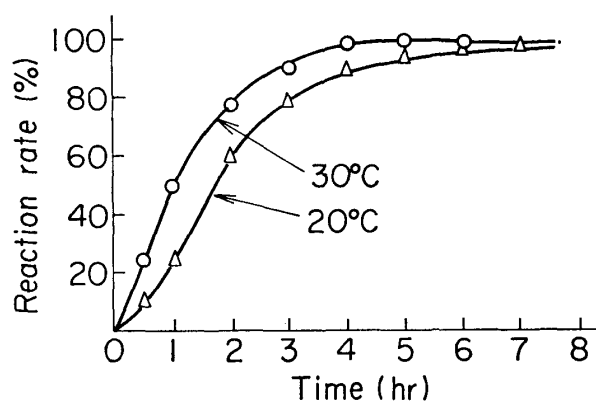
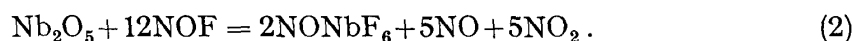
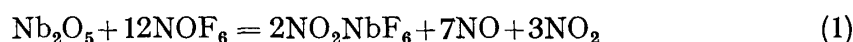


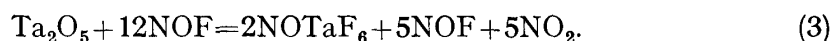
Fig. 1. Disintegration of ore with $N_2O_3 \cdot 12.5HF$

results obtained by 52°, 94° material or 80 mole% HF-20 mole % NO_2 solution and that of $N_2O_3 \cdot 12.5 HF$ as shown in Fig. 1.

In the preceding experiments on the disintegration of the ore, the behaviour examined for each oxide constituting the specimen with solvents. First, it was found that the reaction of Nb_2O_5 with the Nitrofluor process solvents gives white solid product which has poor solubility in each solution. Chemical analysis showed that the composition of this product with $N_2O_3 \cdot 12.5 HF$ is very close to that of nitylium hexafluoroniobate, while those with the other solvents were very close to nitrosylium hexafluoroniobate. Therefore, the possible reactions are:



Ta_2O_5 also formed white precipitates similar to the case of Nb_2O_5 with any Nitrofluor process solvent, and the chemical compositions almost agree with that of nitrosylium hexafluorotantalate. The reaction considered is:



It is known that $V^{(2)}$, $Ge^{(3)}$, $As^{(3)}$, $Se^{(3)}$, $Mo^{(4)}$, $Sb^{(3),(5)}$, $W^{(4)}$, and $U^{(4)}$ make nitylium salt as equation (1), and $Be^{(1)}$, $Ti^{(1)}$, $Zr^{(1)}$, $Si^{(1),(6)}$, $Ge^{(7)}$, $Mo^{(4),(8)}$, $Tc^{(9)}$, $W^{(4),(9)}$, $Re^{(9)}$, $Os^{(9)}$, $Pt^{(9),(10)}$, $U^{(4),(8)}$ make nitrosylium salt as equations (2) and (3). Detailed studies on the crystal structure of some of these nityl and nitrosyl compounds have been developed by X-ray diffraction analysis. Although the same kind of study was attempted to identify the niobium and tantalum com-

(2) H.C. Clark and H.J. Emeleus, J. chem. Soc. (London), (1958), 190.

(3) E.E. Aynsley, G. Hetherington and P.L. Robinson, J. chem. Soc. (London), (1954), 1119.

(4) J.R. Geichman, R.A. Smith and P.R. Ogle, Inorg Chem., **2** (1963), 1012.

(5) D. Cook, S.J. Kuhn and G.A. Olah, J. chem. Physics, **33** (1960), 1669.

(6) O. Giemser und U. Biermann, Chem. Ber., **100** (1967), 1184.

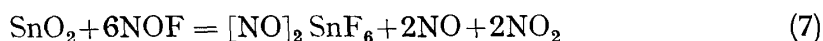
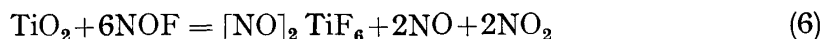
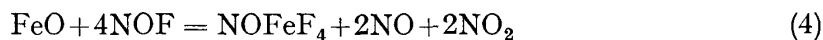
(7) P. Bouy, Ann. Chimie, **4** (1959), 853.

(8) J.R. Geichman, E.A. Smith, S.S. Trond and P.R. Ogle, Inorg. Chem., **1** (1962), 661.

(9) J.H. Holloway and H. Selig, J. inorg. nuclear Chem., **30** (1968) 473.

(10) F.P. Gortsema and R.H. Toeniskoetter, Inorg. Chem., **5** (1966), 1217.

pound, no clear result was obtained because of their high hygroscopic quality. However, the materials obtained are believed to be nitryl and nitrosyl compounds according to chemical analysis as mentioned above. The reactions of the solvent with the other components are as follows:

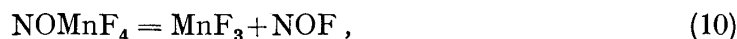


The solubility of the metal complex fluorides was measured in the Nitrofluor process solvents. The results obtained are shown in Table 2. The minimum value of the solubilities of iron and manganese are given in Table 2 because the data varied widely under the present test conditions. Presumably, the poor reproducibility is

Table 2. Solubility of complex fluoride, (g/100 cc, 20°C)

	80 Mole % HF- 20 Mole % NO ₂	52° Material	N ₂ O ₃ ·12.5 HF (68° Material)	NOF·3.1 HF (94° Material)
Nb	1.34	1.52	0.96	0.99
Ta	1.95	2.13	1.66	0.98
Fe	4.2	2.5	4.5	6.7
Mn	1.3	1.0	1.1	1.5

attributed to the fact that these complex fluorides formed as equation (4) and (5) tend to dissociate into insoluble fluorides as the following reactions:



and also to the fact that the degree of dissociation is sensitive to the condition of the solution. Another solubility data were obtained roughly with the Nitrofluor process solvents: titanium and tin: by scores of grams per 100 cc solution and silicon: by hundreds of grams per 100 cc solution around room temperatures.

The chemical composition of the solid product obtained from the reaction of the ore specimen with N₂O₃·12.5 HF followed by the centrifugal separation of the solution is given in Table 3-①. As is obvious from this result, niobium and tantalum concentrated into the precipitate, and subsequent solution is accumulated with titanium, tin, iron and manganese. This result appears to be as expected from the difference of the solubilities of the components. When N₂O₃·12.5 HF was used 1.25 times as much as the theoretical quantity in the disintegration of the ore specimen as described before, the amount of niobium and tantalum lost into the dissolver solution were about 0.3 and 2% of the original quantities, respectively.

Table 3. Result of decontamination

	Condition of volatilization			Composition (%)							
	Gas concentration	Temp. (°C)	Time (hr)	Nb	Ta	Fe	Mn	Ti	Sn	Si	F
①	(disintegration)			30.23	5.50	1.69	0.75	0.05	0.06	0.05	44.27
②	HF, 50 wt %	400	4	34.65	6.43	0.02	0.004	-	0.03	-	46.60
③	N ₂ O ₃ ·12.5HF, 18 "	300	2	35.98	1.12	0.008	0.005	-	0.002	-	44.87
④	" "	410	4	27.89	12.78	0.32	0.13	0.02	0.01	-	42.82
⑤	" 29 "	300	2	35.88	1.28	0.008	0.005	0.0003	0.001	-	44.84
⑥	" "	410	4	28.94	11.37	0.23	0.09	0.017	0.008	-	43.04
⑦	" "	300	16	34.94	2.56	0.07	0.05	-	0.016	-	44.61
⑧	" "	410	4	20.32	23.77	0.57	0.23	0.038	0.019	-	40.83
⑨	" 18 "	330	2	36.40	0.45	0.02	0.016	-	0.005	-	44.99
⑩	" "	410	4	25.44	16.96	0.09	0.03	0.005	0.003	-	42.03
⑪	" 29 "	330	2	35.66	1.55	0.04	0.02	0.0003	0.008	-	44.80
⑫	" "	410	4	23.44	19.98	0.08	0.03	0.006	0.004	-	41.49

III. 2 Purification by sublimation

Although further decontamination of the preceding solid product is achieved by washing with the solvent according to the difference of solubilities, the dissolution loss of niobium and tantalum would not be avoided as mentioned above. Therefore, the purification of the solid product by sublimation was tried. This separation

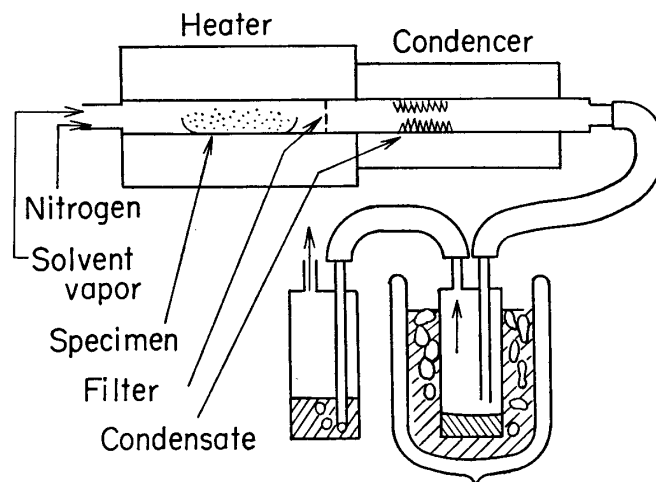


Fig. 2. Experimental apparatus for selective sublimation

method studied involves the volatile transfer of complex fluorides of niobium and tantalum contained in the solid product whose composition is given in Table 3-① in the presence of HF gas or the vapor from N₂O₃·12.5 HF using the apparatus sketched in Fig. 2. The chemical composition of the condensate originated by the volatile separation at 400°C with HF-N₂ gas (50wt%) is given in Table 3-②. This condensate was highly hygroscopic and colorless needleshaped crystal, and fairly high purity. The niobium and the tantalum compound constituting the condensate were identified with the products of the equation (1) and (2), respectively.

III. 3. Separation of niobium and tantalum

The sublimation of the complex fluorides of niobium and tantalum obtained by the reaction of the metals with the Nitrofluor process solvents were measured in nitrogen atmosphere utilizing the thermobalance. The results are shown in Fig. 3, and it was found that the niobium compounds generally tend to sublimate at lower temperatures than the tantalum compounds and that especially the maximum temperature difference was observed when the compounds were prepared with $N_2O_3 \cdot 12.5 HF$. As already described, the main reaction product of niobium

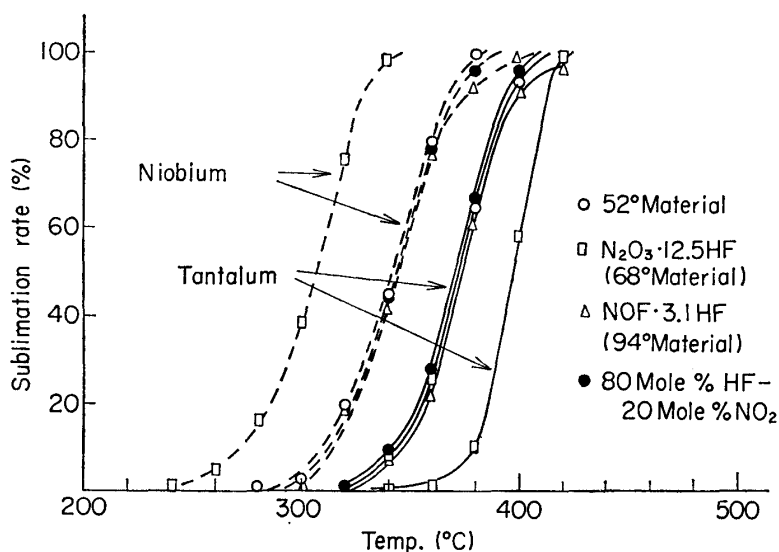


Fig. 3. Sublimation of niobium and tantalum complex fluoride, (in nitrogen)

with $N_2O_3 \cdot 12.5 HF$ is nitylium hexafluoroniobate as shown in equation (1), whereas the main reaction products with the other solvents are nitrosylium hexafluoroniobate as shown in equation (2). On the other hand, the reaction of tantalum with any Nitrofluor process solvents provides mainly nitrosylium hexafluorotantalate as shown in equation (3). Presumably, the behaviour of the niobium and tantalum compounds obtained by $N_2O_3 \cdot 12.5 HF$ is attributed to the difference of nityl and nitrosyl compounds. Then, experiments on the possibility of separating niobium and tantalum from each other by fractional sublimation was performed.

An artificial sample containing about the same quantity of niobium and tantalum was prepared by the reaction of the metals and $N_2O_3 \cdot 12.5 HF$. Four types of experiments were tried utilizing the apparatus as shown in Fig. 2 described before. The results obtained in a carrier gas of nitrogen are shown in Table 4. In this table, R and C denote the amount of the remnant and the condensate, respectively. The R and the C with suffix of Nb or Ta indicates each content of the remnant and the condensate. As can be seen in the result, the ratio of niobium to tantalum was less than 1 in the remnants and was slightly greater than 1 in the condensates. These results show that for the separation the niobium tends to

Table 4. Niobium-tantalum separation in nitrogen

Temp. (°C)	Time (hr)	R/C	R _{Nb} /R _{Ta}	C _{Nb} /C _{Ta}
290	2	3.34	0.80	2.18
"	16	0.35	0.49	1.27
310	2	2.26	0.59	3.79
"	4	0.59	0.53	1.44
330	2	1.47	0.46	3.38
"	8	0.34	0.178	1.62
"	16	0.117	0.38	1.11
340	2	0.93	0.35	2.62
"	16	0.040	0.71	1.01
350	2	0.97	0.31	3.08
"	8	0.197	0.061	1.42
360	2	0.74	0.33	2.18

Table 5. Niobium-tantalum separation in HF vapor

Temp. (°C)	Time (hr)	R/C	R _{Nb} /R _{Ta}	C _{Nb} /C _{Ta}
280	2	5.25	0.76	6.04
"	8	1.62	0.41	5.20
"	16	1.27	0.54	2.22
290	2	1.46	0.92	1.13
"	16	0.44	0.40	1.46
300	2	0.45	0.42	1.45
"	8	0.146	0.27	1.18
310	2	0.29	0.83	1.05
"	8	0.053	0.074	1.09
320	2	0.143	0.36	1.14
"	8	0.031	0.0189	1.06
"	16	0.006	0.20	1.01

sublimate preferentially in the presence of nitrogen though the effect was not as satisfactory as expected.

So the HF gas was tested next as the carrier gas. The results are shown in Table 5. A slightly higher enrichment of niobium than that of the former case was observed in an initial condensate at a relatively lower temperature. The results obtained with the vapor from $N_2O_3 \cdot 12.5HF$ of various concentration as a carrier gas are shown in Table 6. As is shown in this Table, a fairly good improvement in concentrating the niobium and the tantalum into the condensate and the remnant, respectively was achieved under some conditions studied.

Further experiments on the separation with the vapor from $N_2O_3 \cdot 12.5HF$ were performed with the solid product from the ore. The composition of the specimen is shown in Table 3-① as previously described. The results with a dash on a number are those obtained by sublimation of the remnant of the experiment with a corresponding number.

As can be seen in these results, the selective sublimation of niobium and tantalum from the solid product obtained by disintegration of the ore specimen was not as satisfactory as expected though the removal of iron, manganese,

Table 6. Niobium-tantalum separation in N_2O_3 -12.5 HF vapor

Gas concentration (wt %)	Temp. (°C)	Time (hr)	R/C	R_{Nb}/R_{Ta}	C_{Nb}/C_{Tb}
2	290	2	3.24	0.59	10.4
10	"	"	7.31	0.77	25.6
18	"	"	5.05	0.67	89.0
29	"	"	5.48	0.69	79.0
47	"	"	5.72	0.71	69.0
2	"	16	0.48	0.09	2.33
10	"	"	1.46	0.62	2.04
18	"	"	2.23	0.46	9.68
29	"	"	1.66	0.41	5.22
47	"	"	1.33	0.44	5.00
2	300	2	2.43	0.53	6.56
10	"	"	7.66	0.82	7.11
18	"	"	3.51	0.56	93.0
29	"	"	3.29	0.54	128.5
47	"	"	6.51	0.74	109.0
2	"	4	1.46	0.27	10.7
10	"	"	1.15	0.13	16.4
18	"	"	1.78	0.30	54.8
29	"	"	1.84	0.31	68.8
47	"	"	2.13	0.38	49.5
2	"	16	0.24	0.31	1.29
10	"	"	0.54	0.137	2.39
18	"	"	0.34	0.117	1.74
29	"	"	0.26	0.038	1.64
47	"	"	0.40	0.066	2.07
2	330	2	0.80	0.118	4.40
10	"	"	0.82	0.24	2.99
18	"	"	1.15	0.189	8.27
29	"	"	1.79	0.36	11.38
47	"	"	2.11	0.51	5.46
2	"	16	0.067	0.26	1.08
10	"	"	0.111	0.183	1.17
18	"	"	0.29	0.071	1.67
29	"	"	0.31	0.041	1.79
47	"	"	0.24	0.049	1.55

titanium and tin was possible. However, it is evident that more detailed study on the separation of niobium and tantalum remains to be performed from the fundamental view-point.

IV. Summary

The Nitrofluor process offers a method of disintegrating the columbite, volatilizing the niobium and tantalum, and even a possibility of separating them from each other by a nonaqueous inorganic solvent and its vapor. A general conception which was induced from the present study is summarized in a flow-sheet for typical niobium and tantalum ore as shown in Fig. 4.

The main process streams of the course ① is adopted when the mixed complex fluoride of niobium and tantalum is required. For this purpose any Nitrofluor process solvent is useful. The mixed complex fluoride of niobium and tantalum

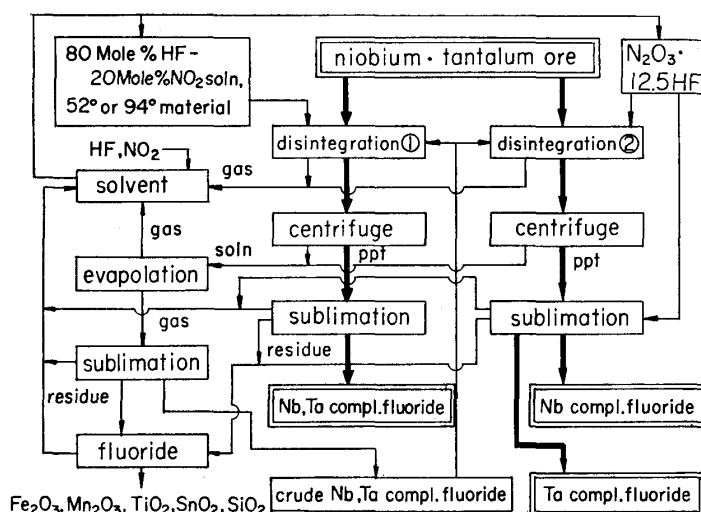


Fig. 4. Flowsheet for treating Nb, Ta ore

is obtained by disintegrating the ore with the solvents followed by separating the dissolver solution centrifugally and volatilizing from the solid product. A small quantity of the niobium and tantalum involved into the dissolver solution is recovered and returned to the course ①. When the complex fluorides of niobium and tantalum are required separately, the main process streams of the course ② appears to be applicable. The characteristic reactions of $N_2O_3 \cdot 12.5HF$ both in the disintegration and the sublimation are expected to be effective in this course. However, as mentioned above, it is obvious that many studies will have to be performed with various techniques of selective manner before a final evaluation can be made. It is possible to recover every component in the solvent consumed through all the process as described in the previous report. For instance, fluorine fixed in FeF_3 , MnF_3 and so on is recovered as HF when the fluorides are treated with air containing some H_2O vapor. The complex fluoride of niobium and tantalum can be converted easily into the potassium double salt because of the high solubility of the complex fluoride in water. Therefore, consequent reduction of the compounds into metallic form is based on a known method, but a new direct reduction method of the complex fluorides remains to be developed because of their peculiarity.

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