SEPARATION OF Ta AND Nb BY EXTRACTION

WITH SEC-OCTANOL-HF-H$_2$SO$_4$ SYSTEM [①]

Chen Huifang, He Wannian, Zhang Yuqi

Beijing General Research Institute for Nonferrous Metals, Beijing 100088

ABSTRACT Research work for the technology of separation of Ta and Nb with extraction by means of secondary octanol-HF-H$_2$SO$_4$ system has been conducted. When the material acidity was HF 4 mol/L and H$_2$SO$_4$ 4 mol/L, the distribution ratios of Ta and Nb were 15.0 and 3.2 correspondingly, and Ta and Nb were extracted simultaneously into the organic phase; while at a lower acidity, the sec-octanol system has a stronger extracting power for Ta than for Nb. When the material acidity was HF 1 mol/L and H$_2$SO$_4$ 1.5 mol/L, the distribution ratios of Ta and Nb were 6.85 and 0.032 respectively, and the separation coefficient went up to 214, which resulted in a good separation of Ta and Nb.

Key words sec-octanol Ta Nb extraction

1 INTRODUCTION

In the ore Ta and Nb always coexist, and the technical methods of separation of Ta and Nb are often solvent extraction in HF-H$_2$SO$_4$ system, with cyclo-hexanone, MIBK[1-3], TBP[4,8] and acetylamine as the extraction solvents. MIBK has good extracting power and selectivity for Ta and Nb, but it is liable to evaporate and has a greater solubility in water, which will cause a greater loss of the organic phase. TBP has a considerable specific gravity and its phase separation is not clear-cut; sometimes it makes phase exchange and leads to a product with high phosphorous content especially when the ambient temperature is high. Hence, we adopt sec-octanol as the extraction solvent, which behaves well in the separation of Ta and Nb in HF-H$_2$SO$_4$ system. This technology has been widely used in China for extraction of the minerals containing Ta and Nb to manufacture products of commercial as well as high purities.
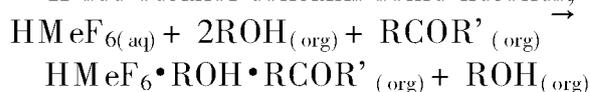
2 PHYSICAL CONSTANTS AND EXTRACTION MECHANISM OF SEC-OCTANOL

Physical constants of sec-octanol used in this technology are: b.p. 174~184 ℃, sp. gr. d_4^{20} = 0.82, viscosity 13.4 cP (20 ℃), refractive index n_D^{20} = 1.425 2, f.p. − 60 ℃, flash point 73 ℃, the content of methyl heptyl-ketone < 12%. The authors have investigated the mechanism of extraction in the sec-octanol-HF-H$_2$SO$_4$ system[9]. When pure sec-octanol is used:

$HMeF_{6(aq)} + 2ROH_{(org)} \xrightarrow{} HMeF_6 \cdot 2ROH_{(org)}$
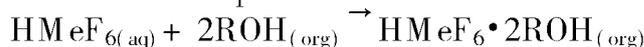
If sec-octanol contains some ketones,

$HMeF_{6(aq)} + 2ROH_{(org)} + RCOR'_{(org)} \xrightarrow{}$
$HMeF_6 \cdot ROH \cdot RCOR'_{(org)} + ROH_{(org)}$

This mechanism belongs to substitution-extraction synergistic mechanism, while that of

$HMeF_6 \cdot 2ROH_{(org)} + RCOR'_{(org)} \xrightarrow{}$
$HMeF_6 \cdot 2ROH \cdot RCOR'_{(org)}$
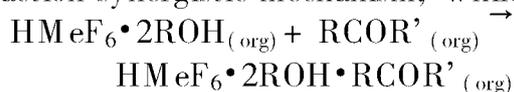
belongs to addition-extraction synergistic action.

The extraction of Ta and Nb with pure sec-octanol forms solvated extract $HMeF_6 \cdot 2ROH$. The local product of sec-octanol contains 10% ~ 15% methyl-heptyl ketone. If ketone-containing sec-octanol is used for extraction they will form two synergistic extracts, $HMeF_6 \cdot 2ROH \cdot RCOR'$ and $HMeF_6 \cdot ROH \cdot RCOR'$.

3 EXPERIMENTAL

3.1 Raw materials

Both tantalum and niobium hydroxides (from Shanghai Yue Long Chemical Works) were 99% pure, soluble in HF and H_2SO_4. Sec-octanol was purchased from the Third Chemical Works of Beijing. Its main content > 85%, methyl-heptyl-ketone < 12% and water < 2%.

3. 2　Experimental method

Extraction was operated in a poly-ethylene separating funnel. After mixed in an electric oscillator for 5 min, the extraction system was set aside for separation, and then the aqueous and organic phases were released individually, waiting for analysis of Ta and Nb.

3. 3　Analytical method

Overall analyses of Ta and Nb: when Ta and Nb were dissolved in HF solution, they formed hydroflouro-complexes. In the MIBK-buty ketone-HF developing agent they had higher distribution ratios. By means of paper chromatography Ta and Nb were separated from Ti, W, Fe, Mn and many other elementary impurities, and then determined by gravimetry. The metallic content in the organic phase was determined by spreading the organic phase on a piece of quantitative paper, undertaking incandescence at 800 ℃, and then weighing the ash.

The separating analyses of Ta and Nb: Ta, Nb and Ti can form different complexes of oxyflouzo-niobium acid, flouro-tantalic acid, etc. In the same developing agent they have different distribution ratios. By means of paper chromatography it is possible to separate Ta and Nb from the impurities, and to determine them by gravimetry.

4　RESULTS AND DISCUSSION

4. 1　Determination of fundamental data in the extraction of Ta and Nb with sec-octanol

4. 1. 1　The saturation capacities of Ta_2O_5 and Nb_2O_5 for sec-octanol

Liquid Ta raw material: Ta_2O_5 152. 8 g/ L, HF 4 mol/ L, H_2SO_4 4 mol/ L;

Liquid Nb raw material: Nb_2O_5 91. 9 g/ L, HF 4 mol/ L, H_2SO_4 4 mol/ L.

Method of manipulation: phase ratio 1: 1,

extraction of sec-octanol with 8 parts of Ta liquid or Nb liquid. The analysis of the organic phase is given in Table 1.

Table 1　The saturation capacity of Ta_2O_5 and Nb_2O_5 for sec-octanol

$[Ta_2O_5]$ /g·L^{-1}	$[H^+]$ /mol·L^{-1}	$[Nb_2O_5]$ /g·L^{-1}	$[H^+]$ /mol·L^{-1}
241. 4	4. 03	152. 65	3. 50

4. 1. 2　Cyclic extraction of Ta and Nb with sec-octanol

Liquid material constituents: (Ta, Nb)$_2O_5$ (Ta: Nb = 1: 1) 102. 25 g/ L, HF 4 mol/ L, H_2SO_4 4 mol/ L; phase ratio 1: 1; cycles taken as: extraction $\rightarrow$ 4 times of pure water back-extraction $\rightarrow$ reextraction. The overall results of 30 cycles are given in Table 2.

Table 2　Cyclic extraction of (Ta, Nb)$_2O_5$ with sec-octanol

Cycle times	3	9	12	15	18
Extraction rate/ %	80. 6	81. 0	80. 5	82. 2	81. 8
Cycle times	21	24	27	30	
Extraction rate/ %	81. 0	82. 0	82. 7	82. 3	

From these results it is known that the times of using sec-octanol have no effect on the extraction rate of (Ta, Nb)$_2O_5$. It can be used cyclically without special treatment. After each cycle it is found that no change of organic phase occurs, with the loss of the organic phase being small.

4. 1. 3　Equilibrium and phase separation time of extraction of Ta and Nb with sec-octanol

Liquid material constituents: (Ta, Nb)$_2O_5$: (Ta: Nb = 1: 1) 158. 70 g/ L, HF 5 mol/ L, H_2SO_4 4 mol/ L; phase ratio 1: 1. The results are given in Table 3.

The results of Table 3 show that the extraction of Ta and Nb with sec-octanol very shortly reaches equilibrium. One minute of mixing will

Table 3　The equilibrium and phase separation time of extraction of (Ta, Nb)$_2O_5$ with sec-octanol

Mixing time/ min	0. 5	1	5	7	10
Phase separation time/ s	20	19	21	23	18
Extraction rate/ %	83. 2	84. 4	85. 5	85. 1	84. 1

give equilibrium, and phase separation is also rapid. From these fundamental experiments it is apparent that the sec-octanol extraction system with HF-H$_2$SO$_4$ will, in all respects, satisfy the requirements of industrial operation. It has good extraction property, low specific gravity, easy phase separation, stability of cyclic use, small loss of organic phase and low cost.

4. 2 Sec-octanol extraction of Ta and Nb

4. 2. 1 Influence of concentration of HF, H$_2$SO$_4$ upon extraction of Ta and Nb

Fig. 1 and Fig. 2 show that, when the concentration of HF is fixed, the extraction rates of Ta and Nb increase with increasing H$_2$SO$_4$. When the concentration of H$_2$SO$_4$ is fixed, the extraction rate of Nb increases with increasing HF, while that of Ta decreases slightly. When the liquid material contains HF 4 mol/L and H$_2$SO$_4$ 4 mol/L, the extraction rates of Ta and Nb are respectively 93. 5% and 80. 0%. The acidity of the decomposition liquid of Ta-Nb ore can satisfy these requirements largely (generally in industrial production HF 6 mol/L, and H$_2$SO$_4$ 4 mol/L), which causes a co-extraction of these ores in organic phase. At low acidities of HF and H$_2$SO$_4$, sec-octanol has much stronger extracting power for Ta than for Nb . When HF is

Fig. 2 Influence of concentration of HF upon the extraction rate of Ta

((Ta, Nb)$_2$O$_5$ 100 g/L, Ta: Nb= 1: 1)
1 —4. 5 mol/L H$_2$SO$_4$; 2 —3. 5 mol/L H$_2$SO$_4$;
3 —2. 5 mol/L H$_2$SO$_4$; 4 —1. 5 mol/L H$_2$SO$_4$;
5 —0. 5 mol/L H$_2$SO$_4$

1 mol/L and H$_2$SO$_4$ is 1. 5 mol/L, the extraction rate of Ta is 82. 0%, that of Nb is 3. 48%, and the separation coefficient is as high as 214, making the separation of Ta and Nb easy.

4. 2. 2 Temperature experiments

Liquid material constituents: (Ta, Nb)$_2$O$_5$ (Ta: Nb= 1: 1) 105. 40 g/L, HF 2 mol/L, H$_2$SO$_4$ 4 mol/L. The experimental results are given in Table 4.

When the extraction takes place at lower temperature (– 4 ℃), separation of phases of the mixture runs slowly after setting aside for 1. 5 min. This might be due to the increase of viscosity of sec-octanol. As the temperature of extraction increases, the separation of phases runs quickly and the extraction rate of Ta

Table 4 The influence of temperature on the extraction rate

t / ℃	Extraction rates / %	
	Ta$_2$O$_5$	Nb$_2$O$_5$
– 4	89. 7	79. 5
0. 5	89. 3	79. 9
17	90. 6	75. 4
37	88. 2	68. 6
45	88. 6	65. 6

decreases slightly, while that of Nb decreases more rapidly. The extraction of Ta and Nb with

Fig. 1 Influence of concentration of HF upon the extraction rate of Ta

((Ta, Nb)$_2$O$_5$ 100 g/L, Ta: Nb= 1: 1)
1 —4. 5 mol/L H$_2$SO$_4$; 2 —3. 5 mol/L H$_2$SO$_4$;
3 —2. 5 mol/L H$_2$SO$_4$; 4 —1. 5 mol/L H$_2$SO$_4$;
5 —0. 5 mol/L H$_2$SO$_4$

sec-octanol-HF-H₂SO₄ system can be operated at any of the ambient temperatures from 0~ 35 ℃.

4. 2. 3   Back-extraction experiment of Nb

From Fig. 1 and Fig. 2 it is shown that, at lower acidity both Ta and Nb have greater separation rates. Nb can be back-extracted into the aqueous phase while Ta remains in the organic phase, making Ta and Nb separate.

The constituents of testing load of the organic phase are: Nb_2O_5 52. 2 g/ L; Ta_2O_5 54. 5 g/ L, H^+ 2. 65 mol/ L. For phase ratio testing, 1 mol/ L H_2SO_4 was used as back-extraction liquid of Nb, and mixing lasted for 5 min. The results are given in Table 5.

From Table 5 it is known that as the phase ratio (O/ W) of back-extraction increases, the back-extraction rate of Ta decreases.

For O/ W = 2/ 1, back-extraction was repeated 5 times. The results are given in Table 6.

From these results it is seen that, when 1 mol/ L H_2SO_4 was taken as the back-extraction liquid of Nb, repeating back-extraction 5 times at O/ W= 2: 1 made Nb go back to the water phase almost completely. In this situation the content of

Table 5   Phase ratio tests for back-extraction of Nb

Phase ratio (O/ W)	Back-extraction rate/ %	
	Ta_2O_5	Nb_2O_5
1: 1	23. 0	96. 0
2: 1	13. 0	86. 0
3: 1	9. 2	74. 3

Table 6   Times tests for back-extraction of Nb

Times	$E^*_{Nb}/\%$	$E^*_{Ta}/\%$	Nb in Ta/ %
1	85. 0	12. 0	16. 2
2	99. 0	21. 8	13. 0
3	> 99. 0	28. 8	0. 062
4	> 99. 0	33. 8	0. 0039
5	> 99. 0	38. 3	0. 0021

*   accumulative back-extraction rate

Nb in Ta became 0. 003 9 % and about 34% of

Ta was back-extracted.

4. 2. 4   The extraction of Ta from Nb liquid

The back-extraction tests of Nb showed that part of Ta was also back-extracted at the same time. Hence, tests were made to extract Ta from Nb liquid. The constituents of Nb liquid are: Nb_2O_5 80. 4 g/ L, Ta_2O_5 21. 9 g/ L, HF 1. 25 mol/ L, H_2SO_4 1 mol/ L. At O/ W= 1: 3 batch extraction was repeated 7 times. The results are given in Table 7. It is seen from Table 7 that, at O: W= 1: 3, repeating batch extraction of Ta 6 times will make Ta in Nb liquid become as low as $\leqslant$0. 03% .

Table 7   Times of extraction of Ta from Nb liquid

Times	$E^*_{Ta}/\%$	$E^*_{Nb}/\%$	Nb in Ta/ %
1	49. 1	3. 25	12. 7
2	80. 5	6. 45	5. 1
3	92. 0	9. 33	2. 2
4	98. 1	11. 99	0. 58
5	99. 5	19. 26	0. 15
6	> 99. 9	16. 29	$\leqslant$0. 03
7	> 99. 9	17. 54	$\leqslant$0. 03

*   accumulative extraction rate

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