Dissolution of Columbite and Tantalite in Acidic Fluoride Media

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The dissolution reactions of Nb and Ta from columbite and tantalite in the aqueous solutions of HF, HF-HCl, NH_4F-HCl, HF-H_2SO_4, and NH_4F-H_2SO_4 were kinetically studied in the temperature range of 333 to 353 K. The presence of both H^+ and F^- in the leachant is necessary for the fast dissolution of columbite and tantalite. The increase in these ion concentrations and the elevation of temperature are effective in increasing the dissolution rate. The initial dissolution rate of Nb from columbite under the conditions employed in this work can be expressed as follows:

$$R_i = k_0 a(\mathrm{H}^+)^{1.2} C(\mathrm{F}^-)^{1.1} \exp(-E_a/\mathrm{R}T)$$

where an apparent activation energy, E_a, ranges from 53.9 kJ mol^{-1} to 65.5 kJ mol^{-1}.

I. INTRODUCTION

BOTH Nb and Ta are metals which have high melting points and are difficult to dissolve with ordinary mineral acids. These metals are important materials in producing alloys, optical glass, condensers, and superconducting magnets.

The principal minerals of Nb and Ta are columbite and tantalite, whose chemical formulae are [Nb_2O_5(Fe, Mn)O] and [Ta_2O_5(Fe, Mn)O], respectively. However, these minerals used in industrial processes usually have a chemical formula of [$(Nb, Ta)_2O_5$(Fe, Mn)O]. The Nb-rich mineral is called columbite, while that of Ta-rich is tantalite. The ores containing these minerals are currently leached in Japan with hydrofluoric acid, followed by solvent extraction, neutralization, precipitation, filtering, drying, and roasting to recover Nb_2O_5 and Ta_2O_5.

Although the leaching of columbite or tantalite is an important step in the hydrometallurgical process of Nb and Ta recovery, only a limited number of studies have been reported. Most minerals containing Nb and Ta are decomposed by hot concentrated hydrofluoric acid. Sometimes concentrated sulfuric or oxalic acids are added to the hydrofluoric acid to achieve better efficiency.[1] Muir and Lloyd studied the leaching of materials containing Nb and Ta with hydrofluoric acid[2,3] and Baram investigated the kinetics of tantalite dissolution in a mixture of hydrofluoric and sulfuric acids.[4] Sato and Kigoshi examined the leaching of columbite in 20 mol pct NO_2-80 mol pct HF solution.[5] Hoberg and Goette studied the influence of mechanical activation on the kinetics of the columbite leaching process.[6] Mechanochemical activation of columbite concentrates was also studied by Batsuev *et al.*[7]

Majima *et al.* studied the dissolution of oxides, such as cupric oxide and hematite, in hydrochloric acid, perchloric acid, and sulfuric acid from a kinetic point of view, and elucidated the role of hydrogen ions and anions on the dissolution reactions. Also they determined the changes of dissolution rates by the addition of various salts.[8,9,10] As a part of oxide dissolution studies, it is interesting to know the leaching mechanism of complex oxide minerals in a weak acid solution. In this study, kinetics of the dissolution of Nb and Ta from columbite and tantalite were studied.

In connection with this, Omori *et al.* examined the solvent extraction of Nb and Ta from hydrochloric acid-hydrofluoric acid mixtures, and found that the extraction characteristics were improved significantly by mixing hydrochloric acid.[11]

The dissolution kinetics of Nb and Ta from columbite or tantalite in acidic fluoride solutions are reported herein.

II. THERMODYNAMIC DATA AVAILABLE FOR THE DISSOLUTION OF NIOBIUM AND TANTALUM

Oxides of Nb and Ta are difficult to dissolve in ordinary mineral acid solutions, as expected from the potential-pH diagrams of the systems of Nb-H_2O and Ta-H_2O.[12] NbO^{3+} and Ta^{5+} readily react with OH^- to form strong hydroxo complexes.[13] However, we cannot discuss quantitatively the dissolution equilibrium of these oxides at this stage due to the lack of solubility data of Nb_2O_5 and Ta_2O_5.

On the other hand, Nb(V) and Ta(V) react with F^- to form hydroxo-fluoro complexes and most of those complexes are soluble in water as stable species.[13]

In the hydrometallurgy of Nb and Ta, the ores containing columbite and tantalite are generally dissolved with concentrated hydrofluoric acid to produce soluble fluorocomplexes of Nb(V) and Ta(V). Hydrofluoric acid used as a leaching agent is a weak acid having an ionization constant of $10^{-3.17}$ at zero ionic strength and 298 K.[14]

Majima *et al.*[8,9,10] pointed out that the acidic dissolution rates of metal oxides, such as CuO and Fe_2O_3, were greatly enhanced by the increase of H^+ activity in the leachant. Anions also play an important role in determining the dissolution rate in concentrated acid solutions. If these findings are also true for the acid leaching of columbite and tantalite, the increase of H^+ activity in the leachant is an important way to improve the dissolution rates of columbite and tantalite. One of the possible methods to increase H^+ ion activity is to add neutral salts such as NaCl to the leachant. However, HF is a weak acid, and thus the H^+ ion activity in the leachant should be controlled by the ionization equilibrium

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of HF, as long as the leaching solution contains HF alone. Therefore, there is a limit to the increase in H^+ ion activity by the addition of neutral salts. The activity of H^+ ions can also be increased by the addition of strong acids such as HCl and H_2SO_4. The addition of mineral acid such as HCl and H_2SO_4 besides HF or other soluble fluoride salts, which are necessary to form soluble fluoro complexes, should be effective in enhancing the dissolution reactions of Nb_2O_5 and Ta_2O_5.

III. EXPERIMENTAL PROCEDURES

The oxides of Nb and Ta used in this study were columbite from Nigeria and tantalite from Australia. Table I shows the results of chemical analysis and Figure 1 illustrates the X-ray diffraction patterns of the samples used. As is clear from this figure, hematite was detected as a main impurity in the columbite sample, while ilmenite was found in the tantalite sample.

Both ores were crushed to pass through a 150 mesh and a fraction of -150 $+200$ mesh of each sample was subjected to the leaching experiments. Plate 1 shows the samples under a scanning electron microscope. The samples were well screened.

The aqueous solutions of HF alone, HF-HCl, NH_4F-HCl, HF-H_2SO_4, and NH_4F-H_2SO_4 mixtures were used as leachants for the leaching of columbite and tantalite in this work. For each experiment the leachant of 0.5 dm^3 was put into a 0.8 dm^3 Teflon separatory flask immersed in the thermostatted water bath. After the temperature of the leachant reached a predetermined constant level of 313, 333, or 353 K, a mineral sample of approximately 5 grams was charged in the leachant to commence the leaching experiment. Agitation during the experiment was done by using a Teflon blade at 800 r min^{-1}, which was sufficient to neglect the mass transfer effect on leaching. Solution samples were periodically withdrawn for chemical analyses of Nb and Ta by atomic absorption spectrophotometry.

Chemicals used in this study were all of reagent grade, and all the aqueous solutions were prepared by using deionized water with specific resistivity of above 5×10^6 ohm cm.

IV. EXPERIMENTAL RESULTS

Before examining the effects of various factors on the dissolution of Nb and Ta from columbite and tantalite in aqueous acidic fluoride solutions, the leaching of these minerals in a 1 mol dm^{-3} HCl solution or 1 mol dm^{-3} NH_4F

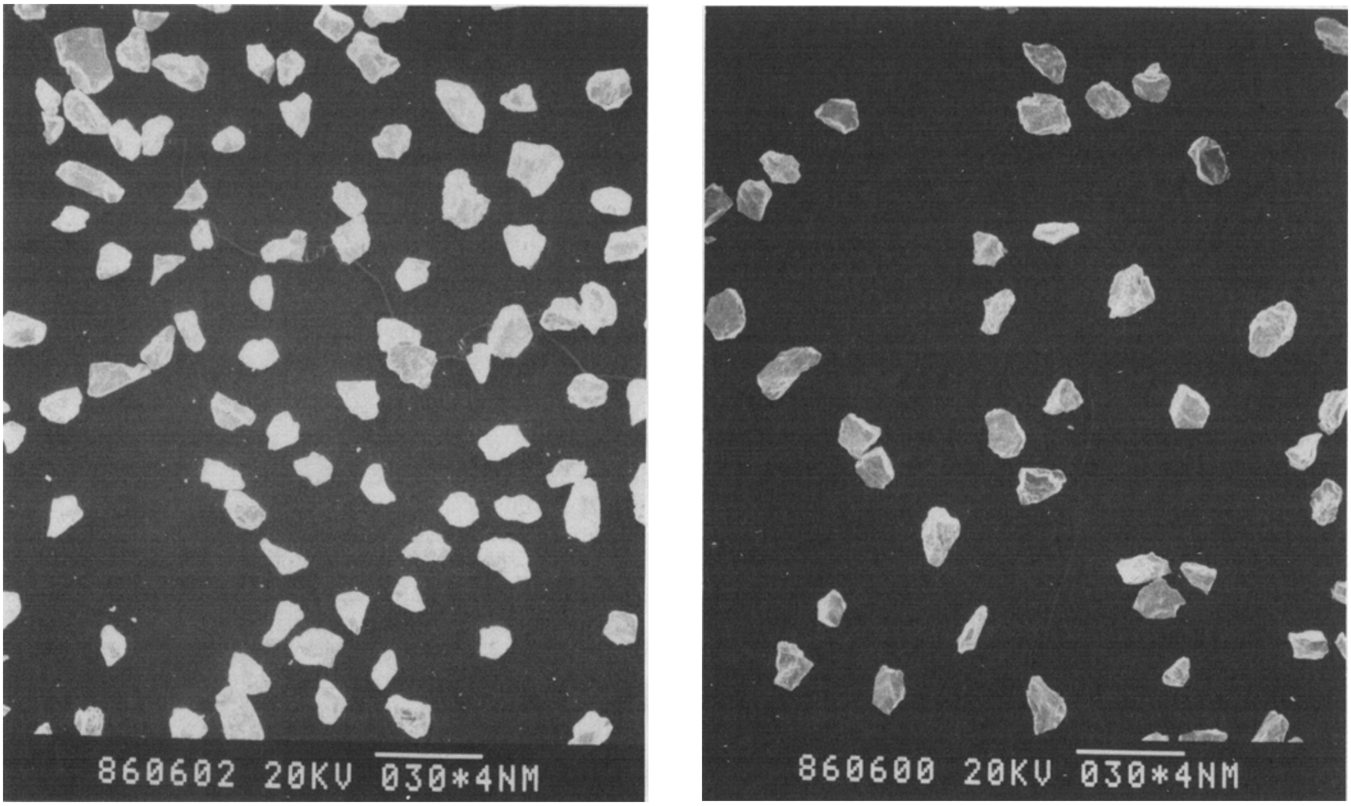

Plate 1 — Particulate samples of columbite (left) and tantalite (right) used for leaching experiments.

Table I. Composition of Mineral Samples

Mineral Sample	Nb_2O_5/Wt Pct	Ta_2O_5/Wt Pct	Fe/Wt Pct	Mn/Wt Pct	Ti/Wt Pct
Columbite	62.19	5.86	16.63	1.83	3.33
Tantalite	41.94	26.83	9.26	7.26	2.55

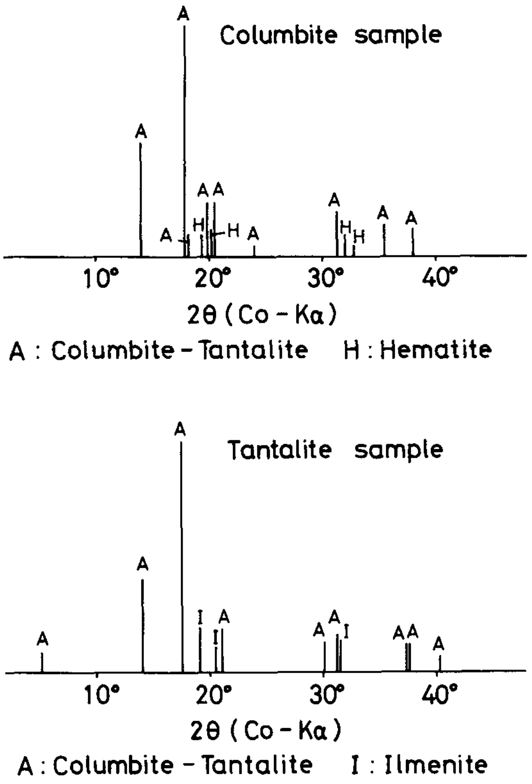

Fig. 1 — X-ray diffraction patterns of mineral samples used.

solution was examined at 353 K. No dissolution of Nb or Ta was detected in these solutions, which suggests that the presence of both H^+ and F^- is essential for the dissolution reaction of Nb and Ta.

To examine the effect of temperature on the dissolution rate of columbite and tantalite in a 10 mol dm^{-3} HF solution, leaching experiments were done at three different temperatures of 313, 333, and 353 K. Figures 2 and 3 depict the results obtained. In these figures dissolution fractions, α, of Nb or Ta from columbite and tantalite were plotted against dissolution time. The dissolution fraction is defined as the ratio of moles of metal dissolved to its total moles contained in a mineral sample. The dissolution rates of Nb and Ta from these minerals increased considerably with increasing temperature. The dissolution fraction of Nb or Ta increased almost linearly with respect to time at a low dissolution fraction, but at a higher dissolution fraction the increase became slower for both metals. Judging from the similar shape of dissolution rate curves of Nb and Ta from columbite or tantalite, the dissolution of Nb and Ta constituents from columbite or tantalite are supposed to behave similarly, although the dissolution of Ta at a low temperature was slightly slower than that of Nb. Therefore, hereafter the dissolution of Nb from columbite was mainly studied.

The initial dissolution rates of Nb and Ta from columbite and those from tantalite were evaluated by fitting the relationship between the dissolution fraction α and time t to Eq. [1] by using a least square method,

$$\alpha = a + bt + ct^2 \qquad [1]$$

and then calculating the slope at $t = 0$, *i.e.*, $(d\alpha/dt)_{t=0}$, as proposed by Dutrizac,[15] since neither the McKewan plot nor the Jander plot was satisfactorily applicable to the present dissolution system. The initial dissolution rate, R_i, thus determined, is equal to the coefficient b in Eq. [1], whose unit is min^{-1}. The R_i was used to analyze the kinetics of dissolution quantitatively. Hereafter, the composition of leachants and the initial dissolution rates for the leaching of Nb and Ta from columbite are summarized in Table II and those from tantalite in Table III, unless otherwise stated.

Dissolution experiments were performed to examine the effect of HF concentration on the dissolution of Nb from columbite at 353 K by changing the concentration of HF from 0.1 to 10 mol dm^{-3}. The initial dissolution rate of columbite greatly increases with increasing HF concentration, as is clear from Table II(a).

On the other hand, a series of leaching experiments was performed to study the effect of HCl on the dissolution of Nb from columbite in 1 mol dm^{-3} HF solutions containing different amounts of HCl at 353 K. The initial dissolution rate

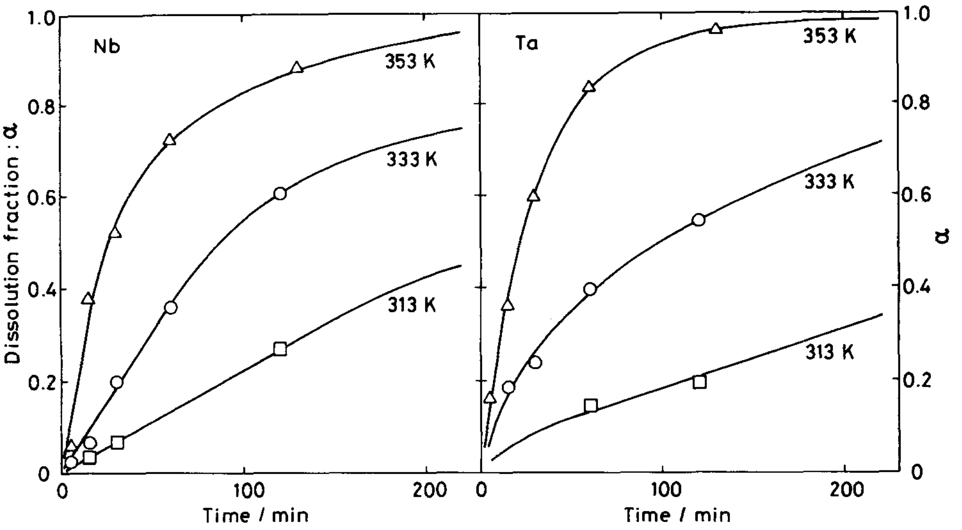

Fig. 2 — Effect of temperature on dissolution rate curves of Nb and Ta from columbite in 10 mol dm^{-3} HF solution.

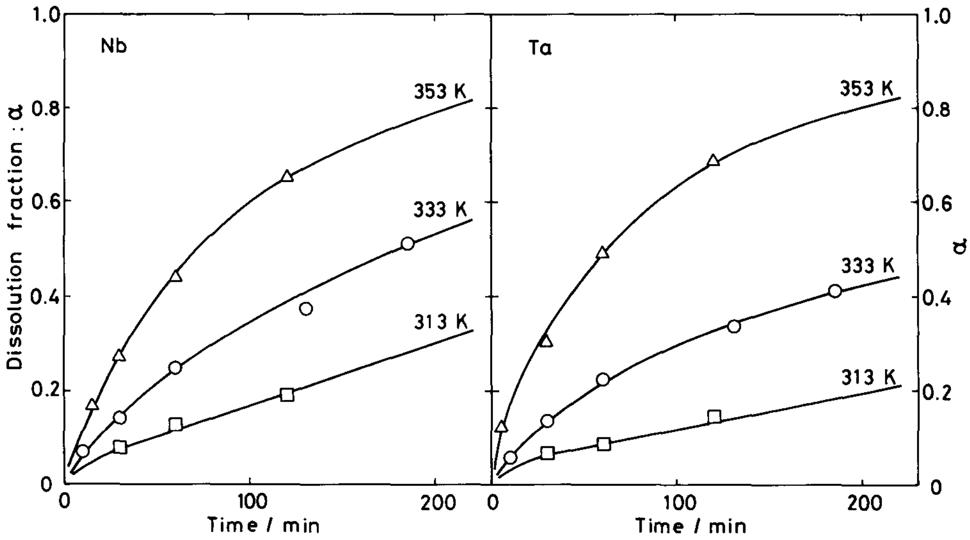

Fig. 3 — Effect of temperature on dissolution rate curves of Nb and Ta from tantalite in 10 mol dm^{-3} HF solution.

of Nb from columbite increased significantly even by the addition of 0.1 mol dm^{-3} HCl, showing almost the same dissolution rate as that in a 2 mol dm^{-3} HF solution. An additional increase in HCl concentration results in the increase in the dissolution rate of Nb although the total F contents in the solutions are the same. The increase in dissolution rate with the addition of HCl suggests that the increase in H$^+$ activity in the leachants is an important way to improve dissolution.

On the other hand, the dissolution rate obtained in a 2 mol dm^{-3} HF-2 mol dm^{-3} HCl solution at 353 K is almost the same as that in a 5 mol dm^{-3} HF solution. This indicates that H$^+$ is a more effective ion than F$^-$ on a concentration basis. Since HF is a weak acid, the concentration of H$^+$ ions would be principally determined by the concentration of HCl. Therefore, the concentration of H$^+$ in a 0.1 mol dm^{-3} HF-1.0 mol dm^{-3} HCl solution would be approximately equal to that in a 1 mol dm^{-3} HF-1 mol dm^{-3} HCl solution. Nevertheless, the initial dissolution rate of Nb from columbite in the former solution is quite different from that in the latter solution, as shown in Table II(a), and this difference is attributed to the difference in HF concentration. The amount of F$^-$ ions in the former solution is inadequate to form fluoro complexes of Nb and Ta contained in the columbite sample and thus the dissolution reaction was slow. These results clearly show the important role of F$^-$ ions, and also that the addition of a strong acid, such as HCl and H_2SO_4, is effective in accelerating the dissolution.

The effect of temperature on the dissolution rate of Nb from columbite in 1 mol dm^{-3} HF-1 mol dm^{-3} HCl solution was examined. The initial dissolution rate of Nb from columbite increased with increasing temperature even in these mixed solutions.

To confirm the important role of a strong acid in the dissolution of columbite, a few additional leaching experiments were performed at 353 K using 1 mol dm^{-3} HF solutions containing different amounts of H_2SO_4. The initial dissolution rate of Nb substantially increases with increasing H_2SO_4 concentration. If one of the roles of HF is to supply F$^-$ ions to form fluoro complexes, other fluoride sources such as NH_4F should be useful. Comparative dissolution experiments were performed at 353 K. The initial dissolution rate of Nb from columbite in 1 mol dm^{-3} NH_4F-1 mol dm^{-3} HCl solution is faster than that in 1 mol dm^{-3} HF solution, but slower than that in 1 mol dm^{-3} HF-1 mol dm^{-3} HCl solution. Hydrofluoric acid is a fluoridizing agent of Nb and Ta but at the same time it plays the role of a H$^+$ ion supplier. It should be noted that HF is an effective H$^+$ ion supplier although it is a weak acid. Therefore, the observation shown in Table II(a) is reasonable.

The concentrations of undissociated HF in the solutions of 1 mol dm^{-3} NH_4F-1 mol dm^{-3} HCl and 1 mol dm^{-3} NH_4F-2 mol dm^{-3} HCl are almost the same. However, the dissolution rates of Nb in the two solutions are significantly different, as shown in Figure 4. Judging from this fact, the direct contributions of H$^+$ and F$^-$ ions instead of the undissociated HF molecule to the dissolution of Nb from columbite is plausible. The concentration of the H$^+$ ion is far larger than that of the F$^-$ ion in 1 mol dm^{-3} NH_4F-2 mol dm^{-3} HCl solution and the concentration of F$^-$ ion is much larger than that of the H$^+$ ion in 2 mol dm^{-3} NH_4F-1 mol dm^{-3} HCl solution. The difference detected among the dissolution rates in these solutions, shown in Figure 4, indicates that the dependency of dissolution rate upon H$^+$ ion concentration is apparently larger than that upon F$^-$ ion concentration.

The effect of F$^-$ ions on the dissolution rate of Nb from columbite was examined. For this purpose, leaching experiments were performed at 353 K in 5 mol dm^{-3} HCl solutions containing NH_4F, by changing the NH_4F concentrations from 0.1 to 0.5 mol dm^{-3} (Figure 5). The dissolution rate of Nb substantially increased with increasing NH_4F concentrations.

To investigate more precisely the effect of H$^+$ concentration on the dissolution rate of Nb from columbite, some leaching experiments were performed in 1 mol dm^{-3} NH_4F

Table II. The Composition of Leachants and the Initial Dissolution Rates of Nb (a) and Ta (b) from Columbite (Concentration Unit: mol dm^{-3})

	Composition of Leachants							
Temp./K	HF	HCl	H_2SO_4	NH_4F	$[F^-] \times 10^{-3}$	$[H^+] \times 10^{-2}$	$a(H^+) \times 10^{-2}$	$R_i/10^{-3}$ min^{-1}
(a) Nb								
313	10	—	—	—	69.7	6.97	6.97	2.46
	1	1	—	—	0.489	100	140	0.303
333	10	—	—	—	56.7	5.67	5.67	7.53
	1	1	—	—	0.323	100	140	1.50
353	0.1	—	—	—	4.47	0.447	0.447	0.0190
	1	—	—	—	14.3	1.43	1.43	0.339
	2	—	—	—	20.3	2.03	2.03	1.61
	5	—	—	—	32.3	3.23	3.23	6.22
	10	—	—	—	45.6	4.56	4.56	27.3
	0.1	1	—	—	0.0209	100	140	0.0570
	1	0.1	—	—	2.04	10.2	10.2	1.42
	1	1	—	—	0.209	100	140	2.95
	1	3	—	—	0.0699	300	1000	4.21
	1	5	—	—	0.0420	500	2770	11.4
	2	2	—	—	0.209	200	472	7.36
	1	—	0.1	—	2.05	10.4	12.4	0.826
	1	—	1	—	0.209	100	158	1.53
	1	—	2	—	0.104	200	410	3.34
	—	0.1	—	1	900	0.00232	0.00232	0.0140
	—	0.5	—	1	500	0.0209	0.0209	0.153
	—	1	—	1	14.4	1.44	1.44	0.889
	—	1	—	2	1000	0.0209	0.0209	0.0950
	—	2	—	1	0.209	100	140	1.23
	—	5	—	0.1	0.00429	490	2690	0.469
	—	5	—	0.2	0.00906	480	2600	1.08
	—	5	—	0.3	0.0134	470	2500	1.56
	—	5	—	0.4	0.0182	460	2410	2.04
	—	5	—	0.5	0.0234	450	2330	3.24
	—	—	1	1	4.90	4.25	4.25	0.662
	—	—	1	2	526	0.0586	0.0586	0.195
	—	—	2	1	0.208	100	158	1.55
(b) Ta								
313	10	—	—	—	6.97	6.97	6.97	1.46
333	10	—	—	—	5.67	5.67	5.67	5.95
353	1	—	—	—	1.43	1.43	1.43	0.393
	2	—	—	—	2.03	2.03	2.03	2.11
	5	—	—	—	3.23	3.23	3.23	8.25
	10	—	—	—	4.56	4.56	4.56	23.4

solution having different contents of HCl (Figure 6). The dissolution rate of Nb from columbite increased with increasing HCl concentration.

The initial dissolution rates for the leaching of Nb from columbite in NH_4F-H_2SO_4 solutions are shown in Table II(a). The results shown in this table indicate a similar tendency observed for the leaching in NH_4F-HCl solutions. It should be noted that the leaching rate at the later stage of leaching in NH_4F-H_2SO_4 solution was slightly smaller than that in NH_4F-HCl solution of the same acid concentration, showing a similar tendency in HF-H_2SO_4 solution.

Since columbite is leached in NH_4F-HCl solution as is in HF solution, some additional leaching experiments on tantalite were done in NH_4F-HCl solutions. The results are depicted in Table III(a) and Table III(b). Similar to the leaching of Nb from columbite, Nb and Ta can be leached from tantalite with NH_4F-HCl solution. Leaching rates of Nb and Ta from tantalite in NH_4F-HCl solution have no significant difference from those in HF solutions.

V. DISCUSSION

The initial dissolution rates at different temperatures were displayed on the Arrhenius plots, as shown in Figure 7(a). The apparent activation energies for the dissolution of Nb and Ta from columbite with 10 mol dm^{-3} HF solution were 56.5 and 65.5 kJ mol^{-1}, respectively.

Similarly, the apparent activation energies for the dissolution of Nb and Ta from tantalite were evaluated by using the initial dissolution rate, as shown in Figure 7(b). In

Table III. The Composition of Leachants and the Initial Dissolution Rates of Nb (a) and Ta (b) from Tantalite (Concentration Unit: mol dm^{-3})

	Composition of Leachants						
Temp./K	HF	HCl	NH_4F	$[F^-] \times 10^{-2}$	$[H^+] \times 10^{-2}$	$a(H^+) \times 10^{-2}$	$R_i/10^{-3}$ min^{-1}
(a) Nb							
313	10	—	—	6.97	6.97	6.97	1.25
333	10	—	—	5.67	5.67	5.67	3.60
353	0.1	—	—	0.447	0.447	0.447	0.009
	1	—	—	1.43	1.43	1.43	0.135
	10	—	—	4.56	4.56	4.56	7.82
	0.1	1	—	0.00209	100	140	0.447
	1	1	—	0.0209	100	140	2.94
	—	2	1	0.0209	100	140	1.85
(b) Ta							
313	10	—	—	6.97	6.97	6.97	0.860
333	10	—	—	5.67	5.67	5.67	3.01
353	0.1	—	—	0.447	0.447	0.447	0.0100
	1	—	—	1.43	1.43	1.43	0.201
	10	—	—	4.56	4.56	4.56	11.5
	0.1	1	—	0.00209	100	140	0.429
	1	1	—	0.0209	100	140	1.80
	—	2	1	0.0209	100	140	1.59

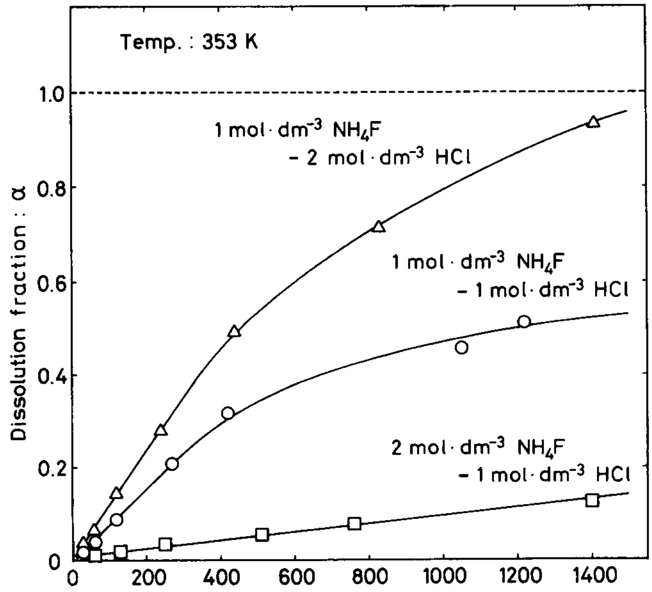

Fig. 4—A comparison of the dissolution rate curve of Nb from columbite in NH_4F-HCl mixed solutions having different compositions.

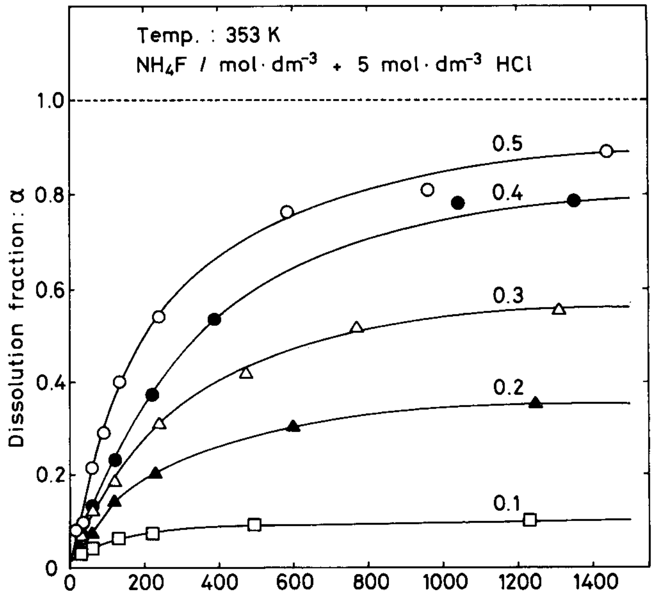

Fig. 5—Effect of NH_4F concentration on the dissolution rate curve of columbite in 5 mol dm^{-3} HCl solutions containing NH_4F.

10 mol dm^{-3} HF solution, those values were 42.7 and 61.1 kJ mol^{-1}, respectively.

The initial dissolution rates of Nb from columbite in 1 mol dm^{-3} HF-1 mol dm^{-3} HCl solution were also displayed on an Arrhenius plot in Figure 7(a). The activation energy of Nb dissolution was found to be 53.9 kJ mol^{-1} and this value is in satisfactory agreement with that in 10 mol dm^{-3} HF solution. Although the addition of HCl to the HF solution results in a substantial enhancement of the rate of the dissolution reaction, no actual change in dissolution mechanism is expected by the addition of HCl.

The concentrations of H^+ and F^- ions in the aqueous solutions of HF alone, HF-HCl, and NH_4F-HCl were calculated at 353 K by using the ionization constant of HF. The value of pK_a at 353 K and zero ionic strength was found to be 3.68 by an interpolation method using the data reported

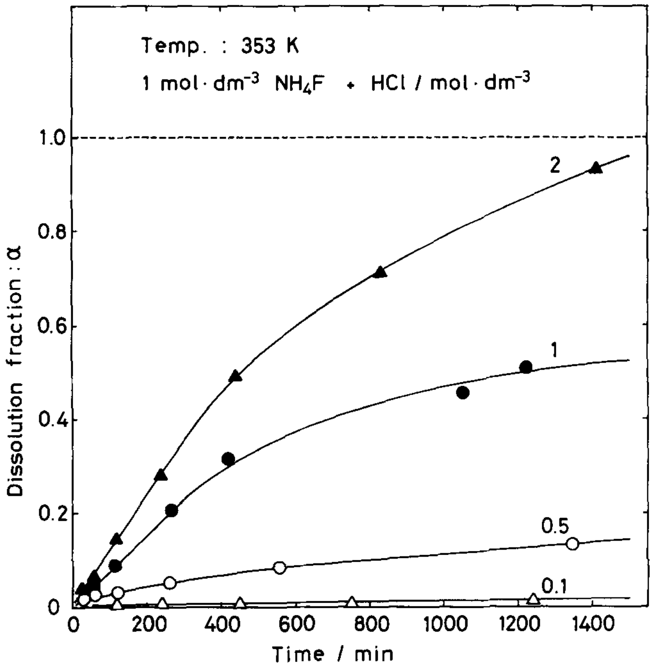

Fig. 6—Effect of HCl concentration on the dissolution rate curve of Nb from columbite in 1 mol dm^{-3} NH$_4$F solutions containing HCl.

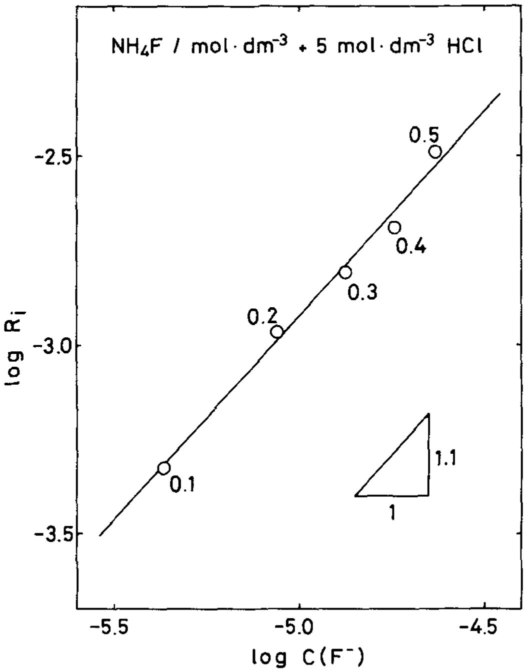

Fig. 8—The dependency of initial dissolution rate of Nb from columbite with respect to the F$^-$ ion concentration.

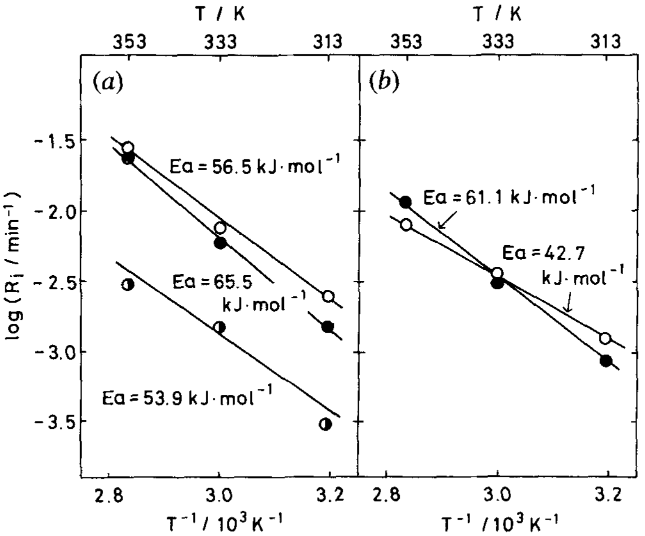

Fig. 7—Arrhenius plots of initial dissolution rates. (*a*) ○: Nb, ●: Ta from columbite in 10 mol dm^{-3} HF solution. ◑: Nb from columbite in 1 mol dm^{-3} NH$_4$F-1 mol dm^{-3} HCl solution. (*b*) ○: Nb, ●: Ta from tantalite in 10 mol dm^{-3} HF solution.

in the literature.[14] Then the effects of H$^+$ and F$^-$ concentrations on the dissolution rate of Nb from columbite were examined.

The initial dissolution rates, R_i, of Nb from columbite in 5 mol dm^{-3} HCl solutions containing various amounts of NH$_4$F at 353 K are plotted against F$^-$ concentration, C(F$^-$), as shown in Figure 8 on a log-log scale. The F$^-$ ion concentration dependency of the initial dissolution rate of Nb from columbite was found to be of the 1.1th order. Then the values of $R_i/\mathrm{C(F^-)}^{1.1}$ were calculated for the data obtained in 1 mol dm^{-3} NH$_4$F solutions containing various amounts of HCl at 353 K and plotted against C(H$^+$) on a log-log scale (Figure 9). The dissolution rate of Nb from columbite is of the 1.3th power with respect to C(H$^+$).

In connection with this, the authors found previously[10] that the activity of the H$^+$ ion instead of the H$^+$ ion concentration is a suitable parameter to analyze the dissolution rate of certain oxides. Anion activity is also an important parameter. However, no reliable method to determine F$^-$ ion activity in a strong acidic solution is available yet. To estimate the values of H$^+$ ion activity in this study, the authors assumed that the a(H$^+$) values of HF-HCl and NH$_4$F-HCl solutions were the same as those in aqueous HCl solutions having the same H$^+$ ion concentration.[9] Similarly, the a(H$^+$) values of HF-H$_2$SO$_4$ and NH$_4$F-H$_2$SO$_4$ solutions mentioned later were assumed to be the same as those in aqueous H$_2$SO$_4$ solution having the same H$^+$ ion concentration.[9] On the other hand, the H$^+$ ion concentrations in HF solutions were sufficiently low, that the H$^+$ ion concentration could be used as H$^+$ ion activity.

Similar plots were made for all the initial dissolution rates of Nb from columbite in aqueous solutions of HF, HF-HCl, NH$_4$F-HCl, HF-H$_2$SO$_4$, and NH$_4$F-H$_2$SO$_4$ by plotting log $R_i/\mathrm{C(F^-)}^{1.1}$ against a(H$^+$) (Figure 10). The concentrations of H$^+$, F$^-$, and the activities of H$^+$ in the mixed solutions of HF-H$_2$SO$_4$ and NH$_4$F-H$_2$SO$_4$ were calculated by using the ionization constants of HF (pK_a = 3.68)[14] and HSO$_4^-$ (pK_a = 2.78)[16] at 353 K. The dissolution rate of Nb is of the 1.2th power with respect to a(H$^+$).

Thus the experimental equation for initial dissolution rate of Nb from columbite can be expressed as follows:

$$R_i = k_0 a(\mathrm{H}^+)^{1.2}\mathrm{C}(\mathrm{F}^-)^{1.1}\exp(-E_a/\mathrm{R}T) \qquad [2]$$

where k_0 and E_a are an initial rate constant and an apparent activation energy, respectively.

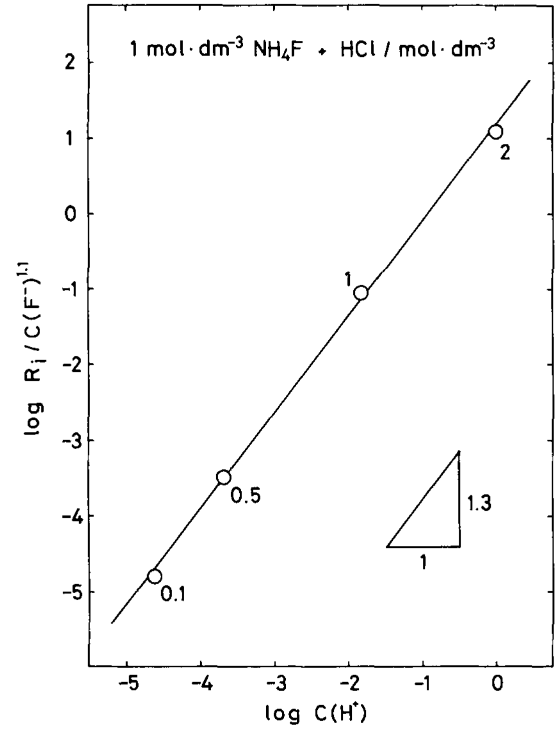

Fig. 9—Relationship between $R_i/C(F^-)^{1.1}$ and $C(H^+)$ for the dissolution of Nb from columbite in 1 mol dm^{-3} NH$_4$F solutions containing different amounts of HCl.

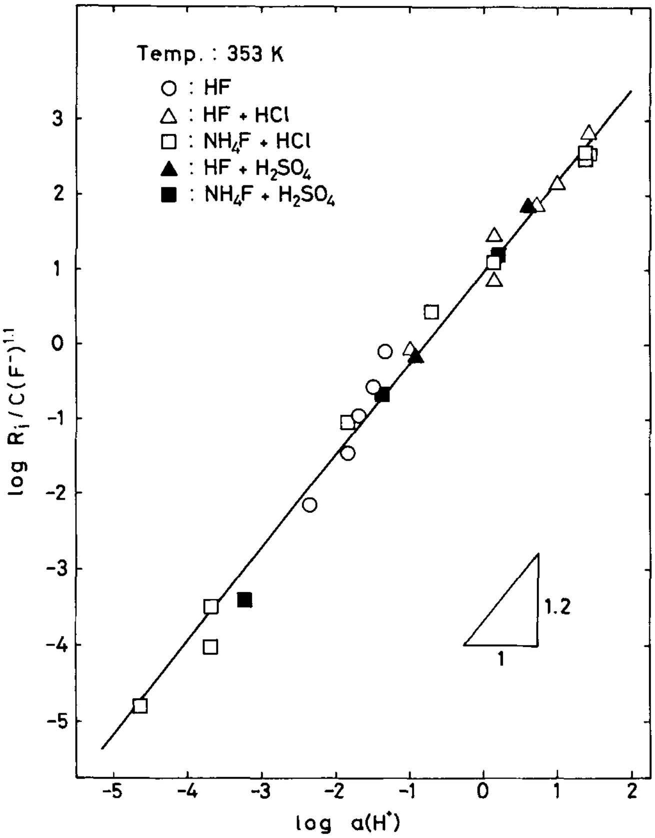

Fig. 10—Relationship between $R_i/C(F^-)^{1.1}$ and $a(H^+)$ for the dissolution of Nb from columbite in acidic fluoride solutions.

As demonstrated previously,[8] anions adsorbed on the oxide surface play an important role in determining the dissolution rate. If this were also true in columbite leaching, the 1.1th power dependency of dissolution rate with respect to F^- ion concentration may refer to the adsorption characteristic of F^- ions on columbite at its low fraction of coverage.

Since there is no way to determine the value of $a(F^-)$ in a strong acid solution at this stage, it is impossible to determine the accurate $a(H^+)$ dependency of Nb dissolution from columbite. The dependency of the dissolution rate of CuO and Fe_2O_3 in HCl solutions was of the first order with respect to $a(H^+)$.[8,9] The 1.2th power dependency of $R_i/C(F^-)$ with respect to $a(H^+)$ found here is close to a first order dependency. These findings suggest that, in the dissolution of Nb from columbite, we can propose a reaction mechanism of H^+ ion attacking on the F^- ion adsorbed on columbite.

Judging from the results obtained in this work, we can conclude that the initial dissolution rate of Nb from columbite is primarily controlled by the activities of H^+ and F^-, and that the other ions, such as SO_4^{2-} and Cl^-, should have only minor importance.

Next, the effects of $a(H^+)$ on the initial dissolution rates of Nb and Ta from tantalite were examined, by plotting the dissolution data on the straight line obtained for the dissolution of Nb from columbite. The result is shown in Figure 11. As is clear in this figure, all the data fall approximately on the straight line indicated, and this result suggests that the $a(H^+)$ dependency of log $R_i/C(F^-)^{1.1}$ was also 1.2. This finding strongly suggests that no difference in dissolution mechanism can be detected between the dissolution of Nb and Ta from tantalite and that of Nb from columbite.

VI. CONCLUSIONS

To elucidate the dissolution mechanism of Nb and Ta from columbite or tantalite in the aqueous solutions of HF, HF-HCl, NH_4F-HCl, HF-H_2SO_4, and NH_4F-H_2SO_4, the dissolution kinetics of Nb and Ta from columbite and tantalite under various experimental conditions were studied in the temperature range of 333 to 353 K.

1. Judging from the similar dissolution behavior of Nb and Ta from columbite or tantalite, there was assumed to be no significant mechanistic difference in their dissolution reactions.
2. The apparent activation energies for the dissolution reactions of Nb and Ta from columbite or tantalite in 10 mol dm^{-3} HF solution and 1 mol dm^{-3} HF-1 mol dm^{-3} HCl mixed solution ranged from 42.7 to 65.5 kJ mol^{-1}. These values suggest that the elevation of temperature is effective in enhancing the dissolution reactions, suggesting the chemical reaction determining mechanism.
3. The presence of both H^+ and F^- ions in a leachant is necessary for the fast dissolution of columbite or tantalite. The increase in these ion concentrations is effective in increasing their dissolution rates.
4. Instead of using a weak acid, HF, as the supplying source of H^+ and F^- ions, HCl or H_2SO_4 and neutral fluoride salt such as NH_4F can be used in combination as a leachant.

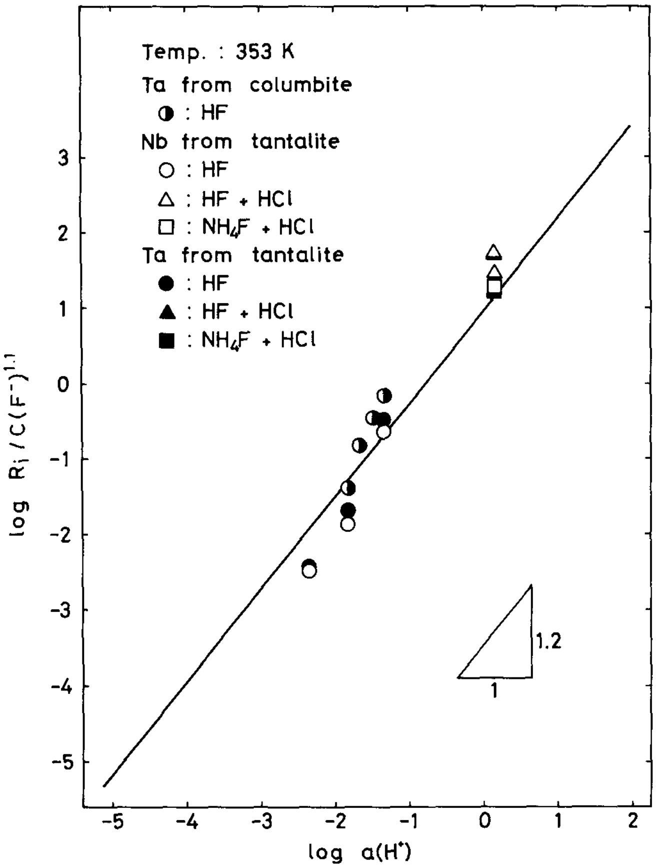

Fig. 11—Relationship between $R_i/C(F^-)^{1.1}$ and $a(H^+)$ for the dissolution of Ta from columbite and those of Nb and Ta from tantalite in acidic fluoride solutions.

5. The experimental equation of initial dissolution rate of Nb from columbite under the conditions in this work can be expressed as follows:

$$R_i = k_0 a(H^+)^{1.2} C(F^-)^{1.1} \exp(-E_a/RT)$$

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