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Dissolution behaviors of Ta_2O_5, Nb_2O_5 and their mixture in KOH and H_2O system

WANG Xiao-hui(王晓辉)[1, 2], ZHENG Shi-li(郑诗礼)[1], XU Hong-bin(徐红彬)[1], ZHANG Yi(张 懿)[1]

1. National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China;
2. Graduate School of Chinese Academy of Sciences, Beijing 100039, China

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Abstract: The dissolution behaviors of Ta_2O_5, Nb_2O_5 and their mixture in KOH and H_2O system were investigated. A $L_9(3^4)$ orthogonal design was used to study the effects of reaction temperature, mass ratio of KOH to Ta_2O_5, and reaction time on the dissolution rate of tantalum. It was found that the effect of reaction temperature on the dissolution rate of tantalum was much greater than that of the other factors. The results of factorial experiments showed that Ta_2O_5 was mainly transformed into insoluble potassium tantalate at low temperature (350 °C) and transformed into soluble potassium tantalate at high temperature (450 °C). The insoluble potassium tantalate was analyzed by XRD, which was proved to be $KTaO_3$. Differently, almost all Nb_2O_5 was transformed into soluble potassium niobate at 350−450 °C. As for the mixture of Ta_2O_5 and Nb_2O_5, the dissolution rate of tantalum increased and the dissolution rate of niobium decreased as an interaction existed between niobium and tantalum. And increasing the mole ratio of Nb_2O_5 to Ta_2O_5 in the mixture was beneficial to the dissolution of both Ta_2O_5 and Nb_2O_5. In addition, the mechanism of the interaction between niobium and tantalum was also investigated through phase and chemical analysis.

Key words: Ta_2O_5; Nb_2O_5; KOH; dissolution behavior; mechanism; solid-solution

1 Introduction

Tantalum and niobium are important rare refractory metals and are widely used in steel, electronic and other high-tech industries[1−3]. The decomposition of the ore is the key step in extracting niobium, tantalum and their compounds from niobium-tantalum ore. At present, the hydrofluoric acid method is widely used in the tantalum-niobium hydrometallurgical industry for the decomposition of the ores[4−6]. However, due to the strong volatility, about 6%−7% of the hydrofluoric acid is lost during the decomposition process, which is harmful to human beings and equipments. As well, a large amount of wastewater containing fluoride is generated which needs to be treated[7−9]. More importantly, this method is only appropriate for high-grade niobium-tantalum ores[10]. Although the resources of niobium-tantalum ores are abundant in China, most of them are in low-grade and difficult to decompose by hydrofluoric acid[11]. Therefore, it is imperative to develop a new and clean production process, so as to achieve optimum resource utilization.

Recently, a new process for the leaching of low-grade niobium-tantalum ores using a KOH roast-water leach system was proposed by the Institute of Process Engineering, Chinese Academy of Sciences, China, with the objective to eliminate fluorine pollution at the source[12]. In this new process, low-grade refractory niobium-tantalum ore is decomposed using KOH molten salt instead of highly concentrated hydrofluoric acid and then is leached by H_2O. The experimental results of the new process show that the decomposition rate for the low-grade refractory niobium-tantalum ore is almost 15% higher than that for the hydrofluoric acid process.

The new process of leaching niobium and tantalum from a low-grade niobium-tantalum ore is under development and there is a general lack of information. Although some studies have been performed on alkali

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Corresponding author: WANG Xiao-hui; Tel/Fax: +86-10-82544856; E-mail: wangxh@home.ipe.ac.cn
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fusion[13−14] and the phase equilibria of Nb_2O_5-K_2CO_3 system and Ta_2O_5-K_2CO_3 system have been given [15−16], no previous work has ever been reported on the fundamental dissolution behaviour of Nb_2O_5 and Ta_2O_5 in KOH molten salt and H_2O system. The aim of this work is to investigate the dissolution behavior of Nb_2O_5, Ta_2O_5 and their mixture in KOH molten salt and H_2O system. And the interaction between niobium and tantalum in the decomposition process was also investigated.

2 Experimental

2.1 Materials

All the chemical reagents employed were of analytical grade and deionized water was used in the corresponding procedures during the experiments. The Nb_2O_5 and Ta_2O_5 samples used for the present study were of reagent grade and were supplied by the Ningxia Orient Tantalum Industry Co., Ltd, China.

2.2 Equipment

The dissolution process was carried out in a 500 mL SUS316 stainless batch reactor equipped with a thermometer, a mechanical stirrer and a reflux condenser. The reactor was heated by immersing in a furnace to reach and maintain the desired temperature within ±2 °C.

2.3 Procedure

All the experiments were conducted in batches. For each run, the required amounts of solid KOH were transferred to the reactor and then were heated to the desired temperature. When the temperature reached the pre-set value and kept stable, the mechanical stirrer was started and a certain amount of Nb_2O_5 (Ta_2O_5 or their mixture) was added to the reactor. The mixture was stirred at a constant speed under an atmospheric pressure. When the reaction time was reached, the products were cooled to room temperature quickly using cold airflow. Under the ambient conditions, the products were leached with a certain amount of water and filtered to obtain a solution and a solid residue. The resulting leaching solution and the residue were analyzed for Nb and Ta by ICP-OES. The dissolution rate (K) of the elements was calculated using the following expression:

$$K=[1-(m_r/m_o)]\times 100\%$$

where m_r and m_o are the mass of the element calculated in the residue obtained in the leaching step and the mass of the element calculated in the Nb_2O_5(Ta_2O_5 or their mixture), respectively. The leaching residues were examined by X-ray diffraction analysis (XRD, using Phillips PW223/30).

3 Results and discussion

When Nb_2O_5 (Ta_2O_5) reacts with potash, K_3NbO_4 (K_3TaO_4) or $KNbO_3$ ($KTaO_3$) forms. When the mole ratio of K_2O to Nb_2O_5(Ta_2O_5)≤1:1, the reaction product is mainly in the form of $KNbO_3$ ($KTaO_3$). And when the mole ratio of K_2O to Nb_2O_5(Ta_2O_5)≥4:3, the reaction product is mainly in the form of K_3NbO_4 (K_3TaO_4). The $KNbO_3$ ($KTaO_3$) is insoluble and cannot be leached by water. By contrast, the K_3NbO_4 (K_3TaO_4) will hydrolyze to soluble $K_8Nb_6O_{19}$ ($K_8Ta_6O_{19}$) and then be leached in the water leaching process. The purpose of our research is to find the optium reaction conditions under which the highest dissolution rate of niobium and tantalum can be obtained. Therefore, the experiments below are all conducted under the condition of mole ratio of K_2O to Nb_2O_5(Ta_2O_5)>4:3.

3.1 Dissolution behavior of Ta_2O_5

3.1.1 Effect of leaching parameters on dissolution of Ta_2O_5 using $L_9(3^4)$ orthogonal design

Through our preliminary experiments, we found that the reaction temperature, mass ratio of KOH to Ta_2O_5 and reaction time are the main parameters affecting the dissolution of Ta_2O_5. Thus, an $L_9(3^4)$ orthogonal design was used to investigate the effect of reaction temperature (T_r), mass ratio of KOH to Ta_2O_5 (R_a) and reaction time (t) on the dissolution rate of Ta_2O_5 in KOH and H_2O system. The variable assignment and the level settings are listed in Table 1. The results of $L_9(3^4)$ orthogonal experiments are presented in Table 2.

Table 1 Experimental factors and levels

Level	Factor		
	T_r/°C	R_a	t/min
1	350	3:1	60
2	400	5:1	180
3	450	7:1	300

In Table 2, K_1, K_2 and K_3 represent the sum of dissolution rate of Ta_2O_5 of level 1, level 2 and level 3 of a factor, respectively. $K_1/3$, $K_2/3$ and $K_3/3$ represent the average of K_1, K_2 and K_3, respectively. R represents the maximum difference value among K_1, K_2 and K_3. The orthogonal experiment results of variance analysis are shown in Table 3.

Table 2 and Table 3 show that the most significant factor is reaction temperature, which is statistically significant at the 99% confidence level. In the selected range, the mass ratio of KOH to Ta_2O_5 and reaction time

Table 2 Results of $L_9(3^4)$ orthogonal experiments

No.	Factor				
	T_r	R_a	t	Error	Dissolution rate of Ta_2O_5/%
1	1	1	3	2	4.12
2	2	1	1	1	47.21
3	3	1	2	3	87.89
4	1	2	2	1	5.29
5	2	2	3	3	46.33
6	3	2	1	2	85.06
7	1	3	1	3	5.65
8	2	3	2	2	46.75
9	3	3	3	1	86.38
K_1	138.120	15.261	137.631	135.831	Total dislocation of Ta_2O_5: 414.68
K_2	136.479	139.191	137.880	137.619	
K_3	139.881	260.031	138.969	141.030	
$K_1/3$	5.020	45.310	45.610	46.407	Mean dislocation: 46.08
$K_2/3$	46.763	46.293	45.973	45.560	
$K_3/3$	86.443	46.623	46.643	46.260	
R	81.423	1.313	1.033	0.847	Order of factors: T_r>>R_a>t

Table 3 Variance analysis of orthogonal experiment results

Factor	Category			
	S	f	F	Prominence
T_r	9 946.767	2	8 099.973	*
R_a	2.801	2	2.281	
t	1.649	2	1.343	
Error	1.230	2	1.000	

$F_{0.01}(2, 2)=99.00$; $F_{0.05}(2, 2)=19.00$

have no significant influence on the dissolution of Ta_2O_5.

3.1.2 Effect of reaction temperature

According to the results of the orthogonal experiments, reaction temperature has much more significant influence on the dissolution of Ta_2O_5 than other factors do. Thus, the effect of reaction temperature was further investigated by factorial experiments under the conditions of reaction time of 1 h and mass ratio of KOH to Ta_2O_5 of 5:1. The results are shown in Fig. 1.

It can be seen from Fig. 1 that the dissolution rate of Ta_2O_5 increases significantly with the increasing reaction temperature. To investigate this phenomenon, the residues obtained after Ta_2O_5 is decomposed by KOH molten salt and dissolved by water were dried at 120 °C for 10 h and then analyzed by XRD. The results are shown in Fig.2. It can be seen from Fig.2 that all diffraction peaks of the insoluble residue are attributable to $KTaO_3$. The XRD pattern is consistent with that reported in JCPDS No.01-077-0917. In order to prove that the $KTaO_3$ is not formed in the water dissolution procedure, we used ethanol instead of water in the water dissolution procedure. There is also $KTaO_3$ in the residue as shown in Fig.2. This indicates that besides converting into K_3TaO_4, a part of tantalum directly converts into insoluble $KTaO_3$ in the KOH decomposition procedure. And this is the reason for the low dissolution rate of Ta_2O_5 under low reaction temperature. From Fig.1 we can also find that higher temperature results in lower conversion rate of insoluble $KTaO_3$. Therefore, increasing the reaction temperature is beneficial to the dissolution of Ta_2O_5. But when the reaction temperature is higher than 540 °C, the dissolution rate of Ta_2O_5 does not change significantly.

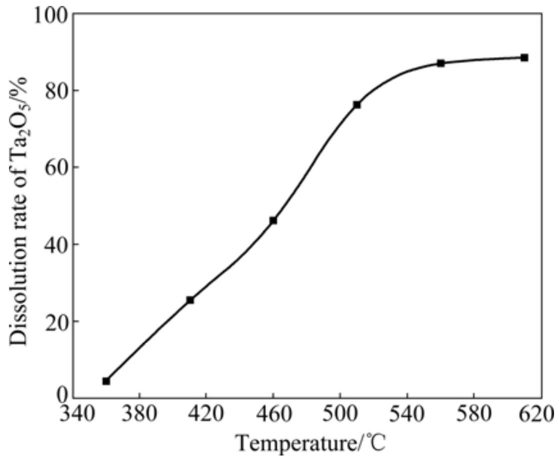

Fig.1 Effect of reaction temperature on dissolution rate of Ta_2O_5 (Reaction conditions: reaction time 1 h and mass ratio of KOH to Ta_2O_5 of 5:1)

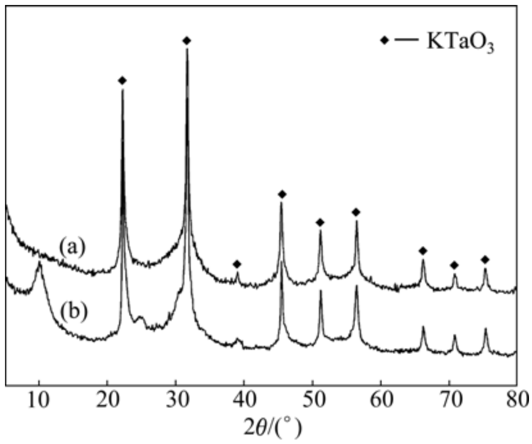

Fig.2 XRD pattern of residue obtained after Ta_2O_5 being decomposed by KOH molten salt and leached by water (a) and ethanol (b)

3.2 Dissolution behavior of Nb_2O_5

The effects of reaction temperature, mass ratio of KOH to Nb_2O_5 and reaction time on the dissolution rate of Nb_2O_5 were examined. The results are listed in Table 4.

Table 4 Effects of reaction temperature, alkaline-to-ore mass ratio and reaction time on dissolution rate of Nb_2O_5

Temperature/ °C	Alkaline-to-ore mass ratio	Leaching time/min	Dissolution rate of Nb_2O_5/%
350	3:1	60	99.25
	3:1	180	98.69
	3:1	300	99.86
	5:1	60	98.69
	5:1	180	98.83
	5:1	300	99.54
	7:1	60	98.92
	7:1	180	99.76
	7:1	300	99.01
400	3:1	30	99.07
	3:1	180	99.68
	3:1	300	99.41
	5:1	30	99.08
	5:1	180	98.81
	5:1	300	99.09
	7:1	30	98.89
	7:1	180	99.74
	7:1	300	99.56
450	3:1	30	99.69
	3:1	300	98.89
	5:1	30	99.70
	5:1	300	99.57
	7:1	30	99.51
	7:1	300	99.04

Table 4 shows that the dissolution rate of Nb_2O_5 is almost 100% in the selected range of reaction conditions, which indicates that most Nb_2O_5 is converted into K_3NbO_4 in the KOH decomposition procedure and then is dissolved by water. This also indicates that the dissolution behavior of Nb_2O_5 in KOH and H_2O system is different from that of Ta_2O_5.

3.3 Dissolution behavior of mixture of Ta_2O_5 and Nb_2O_5

According to the results of the above experiments, the dissolution behaviors of Ta_2O_5 and Nb_2O_5 in KOH and H_2O system are different. Ta_2O_5 converts into K_3TaO_4 and $KTaO_3$ while Nb_2O_5 converts only into K_3NbO_4. As we know, tantalum and niobium often coexist in minerals with the similar properties. Therefore, it is necessary to investigate the dissolution behavior of the mixture of Ta_2O_5 and Nb_2O_5. As the dissolution behaviors of Ta_2O_5 and Nb_2O_5 in KOH and H_2O system are different, when they are mixed together, there may be interaction between them. Therefore, we emphatically investigated the effect of mass ratio of Nb_2O_5 to Ta_2O_5 on the dissolution behavior of the mixture of Nb_2O_5 and Ta_2O_5. The Nb_2O_5 and Ta_2O_5 mixture was obtained through ball-mill mixing of pure Nb_2O_5 and Ta_2O_5. We use mass fraction of Nb_2O_5 to represent the mass ratio of niobium to tantalum in the mixture. The results are presented in Fig.3.

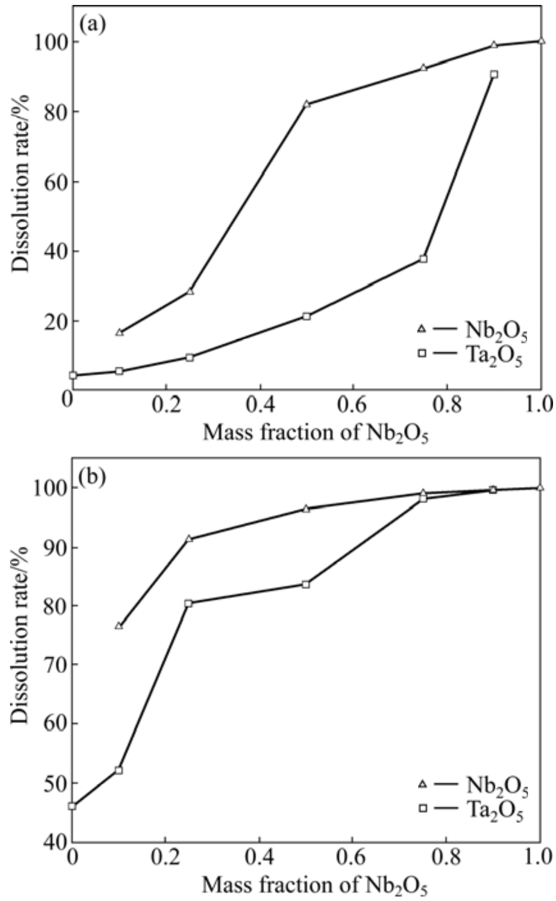

Fig.3 Dissolution behavior of mixture of Ta_2O_5 and Nb_2O_5 in KOH and water system at 350 °C (a) and 400 °C (b) (Reaction conditions: reaction time 1 h and KOH-to- Ta_2O_5(Nb_2O_5) mass ratio 5:1)

From Fig.3. we can see that when the Nb_2O_5 and Ta_2O_5 mixture reacts with KOH and water system, in case that the reaction is carried out at 350 °C and with increasing the mass fraction of Nb_2O_5, the dissolution rate of tantalum increases slowly at first and then rapidly, while the dissolution rate of niobium increases rapidly at first and then slowly. And in case that the reaction is carried out at 400 °C, the dissolution rates of tantalum increase significantly with increasing the mass fraction of Nb_2O_5 in the mixture while the increase of niobium is rather small. This indicates that an interaction exists between niobium and tantalum when Nb_2O_5 and Ta_2O_5 mixture reacts with KOH and H_2O system. The existence of niobium can promote the dissolution of tantalum, while the existence of tantalum can inhibit the dissolution of niobium. To investigate the mechanism of the interaction between niobium and tantalum, phase analysis and component analysis of the residues obtained were made. The results are shown in Fig.4 and Table 5.

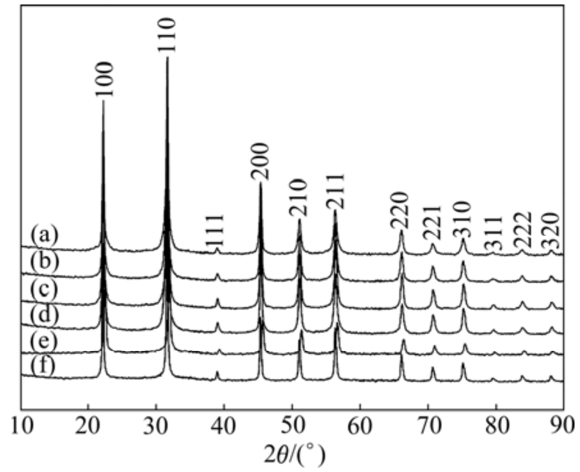

Fig.4 XRD patterns of residues obtained under different reaction conditions: (a) 350 °C, $w(Nb_2O_5)$=0.75; (b) 350 °C, $w(Nb_2O_5)$=0.5; (c) 350 °C, $w(Nb_2O_5)$=0.25; (d) 350 °C, $w(Nb_2O_5)$=0.1; (e) 400 °C, $w(Nb_2O_5)$=0.5; (f) 400 °C, $w(Nb_2O_5)$=0.25

Table 5 Composition of residues obtained under different reaction conditions

No.	Reaction condition		Mole ratio of Ta to Nb in residue
	Temperature/ °C	Mass fraction of Nb_2O_5	
1	350	0.90	0.38:0.62
2	350	0.75	0.63:0.37
3	350	0.50	0.72:0.28
4	350	0.25	0.70:0.30
5	350	0.10	0.86:0.14
6	400	0.50	0.74:0.26
7	400	0.25	0.80:0.20

From Fig.4, we can find that the XRD patterns of the residues are very close to the XRD pattern of $KTa_{0.77}Nb_{0.23}O_3$ (JCPDS No.70-2011), which is a solid solution of $KTaO_3$ and $KNbO_3$. But from Table 5, we can find that the mole ratio of Ta to Nb in the residues are all different from 0.77:0.23, which indicates that the residues are not $KTa_{0.77}Nb_{0.23}O_3$. As we know, the Nb^{5+} and Ta^{5+} are quite similar in chemical properties and ionic radius and there may be isomorphism replacement between Nb^{5+} and Ta^{5+}. $KTaO_3$ and $KNbO_3$ can form continuous solid solution by isomorphism replacement between Nb^{5+} and Ta^{5+}. Thus, we conjecture that the residues of Nb_2O_5 and Ta_2O_5 mixture are $KTaO_3$-$KNbO_3$ solid solutions.

According to Vegard's law[17], the lattice parameter of continuous solid solution has a linear relationship with the mole fraction of one component in it. Therefore, the line of lattice parameter to mole fraction of niobium in the residues is plotted. The results is shown in Fig.5. From Fig.5. we can see that, the relationship between the lattice parameter and mole fraction of niobium is accorded with Vegard's law. This result indicates that the leaching residues of Nb_2O_5 and Ta_2O_5 mixture are really $KTaO_3$ and $KNbO_3$ solid solutions. This result also indicates that when Nb_2O_5 and Ta_2O_5 mixture reacts with KOH, by isomorphism replacement between Nb^{5+} and Ta^{5+}, a part of Nb^{5+} ions enter the crystal lattice of $KTaO_3$, forming $KTaO_3$-$KNbO_3$ solid solution. This is why the leaching rate of Nb_2O_5 decreases when it is mixed with Ta_2O_5. And when the mole fraction of Ta_2O_5 increases (the mole fraction of Nb_2O_5 decreases), more Nb^{5+} ions enter the $KTaO_3$ lattice. Therefore, the leaching rate of Nb_2O_5 decreases with increasing the mole fraction of Ta_2O_5. Similarly, when Nb_2O_5 and Ta_2O_5 mixture reacts with KOH, there may be a part of Ta^{5+} ions entering the lattice of K_3NbO_4, forming K_3NbO_4-K_3TaO_4 solid solution and then may be leached. Therefore, the leaching rate of Ta_2O_5 increases with the increase of Nb_2O_5 mole fraction in the mixture. But as the K_3NbO_4 and K_3TaO_4 are difficult to obtain, further investigation is needed for an in-depth explanation.

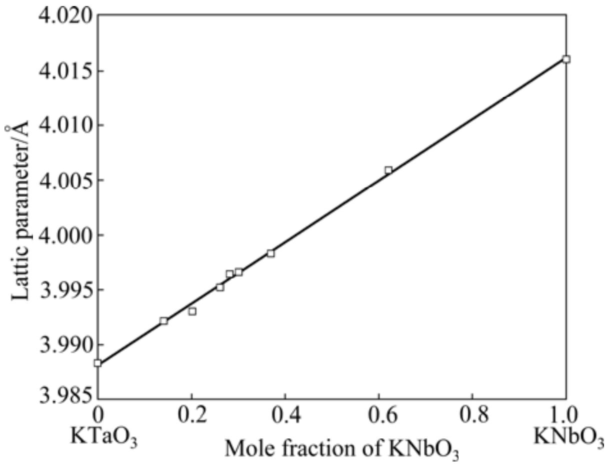

Fig.5 Relation between lattice parameter and mole fraction of Nb

In short, increasing the niobium to tantalum ratio in Nb_2O_5 and Ta_2O_5 mixture is effective for increasing the dissolution rate of niobium and tantalum.

4 Conclusions

1) The dissolution behavior of Ta_2O_5, Nb_2O_5 and their mixture in KOH and H_2O system was investigated. Under the different reaction temperatures, Ta_2O_5 will be

partly converted into K_3TaO_4 and then be dissolved and partly converted into insoluble $KTaO_3$. Increasing the reaction temperature is beneficial to the dissolution of Ta_2O_5.

2) Under the same reaction conditions, Nb_2O_5 will be almost 100% converted into K_3NbO_4 and then be dissolved.

3) When the mixture of Ta_2O_5 and Nb_2O_5 reacts in KOH and H_2O system, by the formation of $KTaO_3$-$KNbO_3$ and K_3NbO_4-K_3TaO_4 solid solutions, the dissolution rate of Ta_2O_5 increases while the dissolution rate of Nb_2O_5 decreases. And increasing the mole ratio of Nb_2O_5 to Ta_2O_5 in the mixture is beneficial to the dissolution of both Ta_2O_5 and Nb_2O_5.

References

[1] MILLER G L. Tantalum and niobium [M]. London: Butterworths Scientific Publications, 1959: 17−66.

[2] FENG Jing-su. The recent advance in applications of niobium [J]. Rare Metal Materials and Engineering, 1994, 23(3): 7−12. (in Chinese)

[3] QU Nai-qin. Properties and applications of Ta/Nb and their alloys [J]. Rare Metals and Hard Alloys, 1998, 133: 48−54. (in Chinese)

[4] EL-HUSSAINI O M. Extraction of niobium and tantalum from nitrate and sulfate media by using MIBK [J]. Mineral Processing and Extractive Metallurgy Review, 2001, 22: 633−650.

[5] HE Chang-yi, LIU Zhi-ming, ZHANG Hao-jun. Treatment of fluorine-containing waste gas from hydrometallurgy of tantalum and niobium ore [J]. Nonferrous Metals, 1998, 4: 141−142. (in Chinese)

[6] LIU Jian-zhong. Current status of China's Ta and Nb initial materials and its countermeasures [J]. Rare Metals and Hard Alloys, 1997, 130: 39−41. (in Chinese)

[7] HE Ji-lin, ZHANG Zong-guo, XU Zhong-ting. Hydrometallurgical extraction of tantalum and niobium in China [J]. Tantalum-Niobium International Study Centre Bulletin, 1998, 93: 1−6. (in Chinese)

[8] XUE Mei. Environmental pollution and treatment of tantalum and niobium hydrometallurgy [J]. Rare Metals and Cemented Carbides, 2005, 33(4): 55−59. (in Chinese)

[9] HAN Jian-she, ZHAO Ming-zhi, WANG Cai-ming, ZHANG Jin, ZHOU Yong. Research on the "Three Wastes" disposal technology for Ta and Nb hydrometallurgy [J]. Rare Metals and Cemented Carbides, 2006, 34(4): 40−44. (in Chinese)

[10] GUPTA C K, SURI A K. Extractive metallurgy of niobium [M]. London: CRC Press, 1994: 98−127.

[11] LIU Jian-zhong, LI Mei-xian. Status and development advices on China's tantalum and niobium resources [J]. Hunan Nonferrous Metals, 1999, 15(3): 60−62. (in Chinese)

[12] WANG Xiao-hui, ZHENG Shi-li, XU Hong-bin, ZHANG Yi. Leaching of niobium and tantalum from a low-grade ore using a KOH roast-water leach system [J]. Hydrometallurgy, 2009, 98: 219−223.

[13] OKA Y, MIYAMOTO M. Extraction of tantalum and niobium oxides from columbite (I): Decomposition of the ore [J]. J Electrochem Soc, 1949, 17: 63−69.

[14] BHATTACHARYA H. Investigations on the analysis of mixed oxides of the elements of Group Va and IVa (Part I): Preparation of pure tantalum and niobium pentoxide from India columbite and their analytical separation [J]. J Indian Chem Soc, 1952, 11(29): 871−875.

[15] ARNOLD R, FREDERIC H. Phase equilibria in the system K_2CO_3-Nb_2O_5 by the method of differential thermal analysis [J]. J Am Chem Soc, 1955, 77: 2115−2119.

[16] ARNOLD R, SOL T, FREDERIC H. Phase diagram of the system $KNbO_3$-$KTaO_3$ by the methods of differential thermal and resistance analysis [J]. Journal of American Chemical Science, 1955, 77: 4228−4230.

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