Leaching of niobium and tantalum from a low-grade ore using a KOH roast–water leach system

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Abstract

A new process is proposed for the leaching and recovery of niobium and tantalum from a low-grade refractory niobium–tantalum ore after adding pure Nb2O5 to adjust the niobium to tantalum ratio. The ore was roasted and decomposed with KOH then leached with water. Experiments were carried out to study the effect of the Nb2O5-to-Ta2O5 mass ratio, decomposition temperature, alkali-to-ore mass ratio and decomposition time on the leaching of niobium and tantalum, as well as the associated impurity elements, such as titanium, iron, manganese, silicon and tin. The optimal conditions were determined to be: Nb2O5-to-Ta2O5 mass ratio 2.33:1; KOH-to-ore mass ratio 2:1; reacting for 60 min at 400 °C. Leaching with water extracted ~95% Nb and 94% Ta together with about 80% Si and Sn, 50% Ti and ~20% Fe and Mn. The niobium and tantalum was recovered as high purity (Nb,Ta)2O5 (99.3%) through evaporation, crystallization and phase transformation processes.

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Niobium–tantalum ore
Alkali roast
Potassium hydroxide
Water leach

1. Introduction

Niobium and tantalum, with high melting points, have been utilized widely in the steel, electronic and other high-tech industries (Miller, 1959; He et al., 1998a). The extraction of these metals from niobium–tantalum ore has been studied for many years and a large number of procedures have been reported. Among these methods, alkali fusion (Eckert, 1995) was the first one to be industrially applied. In this method, sodium hydroxide and sodium carbonate (or the potassium salts) were used as the main reactants. But the shortcoming of this method is the high reaction temperature (typically 800 °C) required. To avoid this disadvantage, a hydrothermal method has been reported (Cardon, 1962; Zelikman and Orekhov, 1965) which requires high pressure and expensive autoclave equipment. Some types of niobium–tantalum ores can also be processed using chlorination (Gupta and Suri, 1994), fusion with ammonium fluoride and bifluoride (Gupta and Suri, 1994), direct acid dissolution with H2SO4 (El-Hussaini and Mahdy, 2002), or a combination of H2SO4 and HF (Krismer and Hoppe, 1984).

Currently, most niobium–tantalum ores are decomposed by concentrated hydrofluoric acid (El-Hussaini, 2001; Gupta and Suri, 1994). However, due to its high volatility, about 6–7% HF is lost during the decomposition process which is hazardous (He et al., 1998a,b). Furthermore, a large amount of wastewater containing fluoride is generated that needs to be treated. More importantly, this method is only appropriate for high-grade niobium–tantalum ores (Miller, 1959). Although the resources of niobium–tantalum ores are abundant in China, most of them are low-grade and difficult to decompose by hydrofluoric acid (Li et al., 1992). Therefore, it is imperative to develop a new and cleaner production process, so as to achieve optimum resource utilization.

Recently, a new process for the leaching of low-grade refractory niobium–tantalum ores with KOH sub-molten salt was proposed with the objective to eliminate fluorine pollution at the source (Zhou et al., 2003). In this process, the ore is decomposed in concentrated KOH solution (sub-molten salt) at atmospheric pressure, giving about 10% higher decomposition than that for the HF process. However, a large amount of KOH solution is required to be evaporated and recycled in this process, which is very energy intensive. In order to optimize this process and reduce the energy consumption, we propose a new process to reduce the amount of KOH.

The new process is based on the decomposition of the ore minerals by molten KOH into K6(Ta,Nb)O19, followed by hydrolysis to soluble K8( Ta,Nb)O16·nH2O which is leached in water according to the following reactions (Ma et al., 1997):

\[
\text{(Fe, Mn)}\text{O} \cdot \text{(Ta, Nb)}\text{O}_3 + 6\text{KOH} = 2\text{K}_3\text{(Ta, Nb)}\text{O}_4 + (\text{Fe, Mn})\text{O} + 3\text{H}_2\text{O}
\]  

(1)

\[
6\text{K}_3\text{(Ta, Nb)}\text{O}_4 + (5 + n)\text{H}_2\text{O} = \text{K}_8\text{(Ta, Nb)}\text{O}_{16} \cdot n\text{H}_2\text{O} + 10\text{KOH}
\]  

(2)

\[
4\text{FeO} + \text{O}_2 = 2\text{Fe}_2\text{O}_3
\]  

(3)
\[ \text{Fe}_2\text{O}_3 + 2\text{KOH} = 2\text{KFeO}_2 + \text{H}_2\text{O} \]  

(4)

\[ 2\text{MnO} + \text{O}_2 = 2\text{MnO}_2 \]  

(5)

\[ \text{MnO}_2 + 2\text{KOH} = \text{K}_2\text{MnO}_3 + \text{H}_2\text{O} \]  

(6)

\[ \text{SiO}_2 + 2\text{KOH} = \text{K}_2\text{SiO}_3 + \text{H}_2\text{O} \]  

(7)

\[ \text{SnO}_2 + 2\text{KOH} = \text{K}_2\text{SnO}_3 + \text{H}_2\text{O} \]  

(8)

\[ \text{TiO}_2 + 2\text{KOH} = \text{K}_2\text{TiO}_3 + \text{H}_2\text{O} \]  

(9)

However, a side reaction also occurs in the decomposition process that produces insoluble \( \text{K(Ta,Nb)}_2\text{O}_3 \) as follows:

\[ (\text{Fe}, \text{Mn})\text{O} \cdot (\text{Ta}, \text{Nb})_2\text{O}_5 + 2\text{KOH} = 2\text{K} (\text{Ta}, \text{Nb})_3\text{O}_3 + (\text{Fe}, \text{Mn})\text{O} + \text{H}_2\text{O} \]  

(10)

Earlier studies (Ma et al., 1997) show that, because of this side reaction, \(< 80\% \) Nb and Ta could be leached by water. Therefore, how to effectively increase the leaching of niobium and tantalum becomes the key in the new process.

Based on our preliminary experiments, we found that increasing the ratio of Nb:Ta in the ore can significantly increase the leach recovery. Therefore, the improved process included first adding a certain amount of Nb\(_2\)O\(_5\) to the ore, then decomposing the enriched ore with solid KOH at about 400 °C and finally leaching the decomposition products with water. After filtration, the alkali-to-ore mass ratio used in this process dropped from 7:1 to 2:1. The general flow sheet of this process is shown in Fig. 1.

The purpose of the present work is to investigate the leaching behavior of niobium, tantalum and other associated mineral impurities such as titanium, iron, manganese, silicon, and tin, and to obtain optimal treatment conditions. Based on all the previous work, the effects of parameters such as the Nb\(_2\)O\(_5\)-to-Ta\(_2\)O\(_5\) mass ratio, decomposition temperature, alkali-to-ore mass ratio, decomposition time and particle size have been investigated. Moreover, the procedures of evaporation, crystallization and phase transformation were also investigated.

### 2. Experimental

#### 2.1. Materials

Potassium hydroxide was of analytical grade (Beijing Chemical Plant) and distilled water was used for leaching experiments. The niobium–tantalum ore sample, Nb\(_2\)O\(_5\) (99.99%) and Ta\(_2\)O\(_5\) (99.99%) were supplied by the Ningxia Orient Tantalum Industry Co. The ore sample was dried, screened and analysed using ICP-OES (PE Optima 5300DV, Perkin Elmer) as shown in Table 1. Mineralogical analysis of the sample was carried out by X-ray diffraction analysis (Phillips PW223/30) and the results indicate that the main crystalline phases in the ore sample are niobite–tantalite and cassiterite (Fig. 2).

#### 2.2. Equipment

The batch reactor used in this work was a 500 mL SUS316 stainless steel container equipped with a thermometer, a mechanical stirrer and a reflux condenser. The reactor was heated by immersing it in a furnace to reach and maintain the desired temperature within ±2 °C.

#### 2.3. Procedures

The Nb\(_2\)O\(_5\)-to-Ta\(_2\)O\(_5\) mass ratio in the ore was adjusted to a specified value by addition of Nb\(_2\)O\(_5\) and mixed homogeneously before decomposition with KOH in the batch reactor. For each run, 100 g solid KOH was first charged into the reactor and then the reactor was heated to the preset value before adding the ore and starting the mechanical stirrer. The mixture was stirred at constant speed under atmospheric pressure; and after reaction, the products were cooled to room temperature quickly using cold air. The products were then leached with water at room temperature and filtered to obtain a solution and a solid residue. The resulting leach solution and the residue were analyzed for Nb, Ta, Ti, Fe, Mn, Si and Sn by ICP-OES.

<table>
<thead>
<tr>
<th>Nb(_2)O(_5)</th>
<th>Ta(_2)O(_5)</th>
<th>SnO(_2)</th>
<th>TiO(_2)</th>
<th>Fe(_2)O(_3)</th>
<th>MnO</th>
<th>SiO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.05</td>
<td>25.00</td>
<td>12.70</td>
<td>4.69</td>
<td>11.76</td>
<td>5.89</td>
<td>2.68</td>
</tr>
</tbody>
</table>

Table 1

Chemical analysis results of the niobium–tantalum ore sample (wt.%).

Fig. 1. Flow sheet for the leaching and recovery of niobium and tantalum.

Fig. 2. XRD pattern of the low-grade niobium–tantalum ore sample.
percentage of the elements leached was calculated using the expression:

\[
\% \text{ leached} = \left(1 - \frac{M_r}{M_o}\right) \times 100\%
\]

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 enriched niobium–tantalum ore, respectively.

3. Results and discussion

3.1. Decomposition of niobium–tantalum ore

3.1.1. Effect of Nb2O5-to-Ta2O5 mass ratio

Fig. 3 shows the results of leaching tests conducted with different Nb2O5-to-Ta2O5 mass ratios in the enriched ore. It can be seen that the recovery of niobium and tantalum increased from 87% to 97% and from 82% to 95% respectively when the Nb2O5-to-Ta2O5 mass ratio increased from 1.08:1 to 4:1. To explain this phenomenon, a phase analysis of the leaching residue from mass ratio 2.33:1 was carried out (Fig. 4) which showed niobium and tantalum mainly in the form of \( \text{KTa}_{0.77}\text{Nb}_{0.23}\text{O}_3 \) (Fig. 3. JCPDS No.70-2011), which is an insoluble solid solution of \( \text{KTaO}_3 \) and \( \text{KNbO}_3 \).

To investigate the formation mechanism of the \( \text{KTaO}_3 \)–\( \text{KNbO}_3 \) solid solution, the reaction behavior of Nb2O5 and Ta2O5 were studied separately. The results showed that when Nb2O5 was reacted with KOH and leached, almost all niobium was leached and no residue obtained. This indicates that the Nb2O5 mainly converts into \( \text{K}_3\text{NbO}_4 \) with no insoluble \( \text{KNbO}_3 \) formed. By contrast, when Ta2O5 was reacted with KOH under the same conditions, only ~46% Ta could be leached and a large amount of residue was obtained, attributable to \( \text{KTaO}_3 \) (Fig. 5 JCPDS 77-0917). These results confirm that the reaction behaviors of Nb2O5 and Ta2O5 in KOH were completely different.

It can be concluded that when niobium–tantalum ore is reacted with KOH, the \( \text{KTaO}_3 \)–\( \text{KNbO}_3 \) solid solution is a result of the formation of \( \text{KTaO}_3 \) and isomorphism replacement between Nb and Ta in the crystal lattice. Similarly, we conjecture that a part of Ta enters the crystal lattice of \( \text{K}_3\text{NbO}_4 \) forming the \( \text{K}_3\text{NbO}_4\)–\( \text{K}_2\text{TaO}_4 \) solid solution, which can then be leached. When the Nb2O5-to-Ta2O5 mass ratio in the ore increased, the amount of \( \text{K}_3\text{NbO}_4\)–\( \text{K}_2\text{TaO}_4 \) increased and \( \text{KTaO}_3 \)–\( \text{KNbO}_3 \) decreased. As a result, the leach recovery of both niobium and tantalum increased. However, when the Nb2O5-to-Ta2O5 mass ratio was larger than 2.33:1, little augmentation was observed and hence the preferred ratio is 2.33:1.

Fig. 3 also shows that the leach recovery of silicon, tin and titanium was quite high due to the formation of soluble \( \text{K}_2\text{SiO}_3 \), \( \text{K}_2\text{SnO}_3 \) and \( \text{K}_2\text{TiO}_3 \) according to the reactions of (7), (8) and (9). Similarly, some soluble \( \text{KFeO}_2 \) and \( \text{K}_2\text{MnO}_3 \) were generated, according to the reactions of (1), (3), (4), (5) and (6), giving 10–20% Fe and Mn in solution.

3.1.2. Effect of decomposition temperature

Fig. 6 shows that increasing of the decomposition temperature was effective in increasing the leaching of Ta, Ti, Fe, Mn and Sn which was...
attributed to increased decomposition rate and diffusion of reactants and products. The recovery of Nb did not change significantly when the decomposition temperature increased from 300 °C to 500 °C. Presumably because the reaction between Nb2O5 and KOH occurs much more readily than other reactions and is complete at only 300 °C. When the temperature was higher than 400 °C, the subsequent leaching of niobium and tantalum was almost constant while that of other impurities still increases. Therefore, a KOH roast temperature of 400 °C is recommended.

3.1.3. Effect of KOH-to-ore mass ratio

The results of leaching tests conducted under different KOH-to-ore mass ratios (Fig. 7) show that the recovery of Nb, Ta, Si, Ti, Sn, Fe and Mn increased with an increase in mass ratio. This may be because of a decrease in the viscosity of the reaction system and mass transfer resistance at the liquid–solid interface. However, little augmentation of Nb and Ta was noted above a mass ratio of 2.0:1 whilst more impurities were leached. Thus, the alkali-to-ore mass ratio of 2.0:1 is recommended.

3.1.4. Effect of roast decomposition time

Table 2 shows the results of leaching tests conducted under different KOH roast times. It can be seen that the recovery of silica decreased with increasing time whilst the recovery of Nb, Ta, Sn, Fe and Mn remained almost constant. According to Zheng (2000), silicon in the ore first forms water-soluble potassium silicate, which then transforms to insoluble silicates during the decomposition process. Therefore, the preferred leaching time was determined to be 60 min.

3.2. Evaporation, crystallization and phase transformation

As the solubility of K8(Ta,Nb)6O19 decreases with increasing KOH concentration in solution, evaporation/crystallization was used to recover the niobium and tantalum from the leach solution. Evaporation of the solution was carried out at 80 °C until the KOH concentration reached about 380 g·L−1, and then the solution was cooled to 30 °C for the crystallization of the K8(Ta,Nb)6O19. The crystallization recovery of niobium and tantalum were 98.8% and 99.0% respectively.

After evaporation/crystallization, the K8(Ta,Nb)6O19 crystals were dissolved in pure water and filtered to remove the insoluble impurities. The phase transformation of K8(Ta,Nb)6O19 was carried out by slowly adding H2SO4 to the solution until the concentration was about 10 wt.%, and then stirring at 80 °C for 30 min. The reaction of K8(Ta,Nb)6O19 and H2SO4 takes place according to reaction (11).

\[
K_8(Ta,Nb)_{6}O_{19} + 4H_2SO_4 = 3(Nb, Ta)_{2}O_{5} \cdot (x/3)H_2O_4 + 4K_2SO_4
\]

The hydrous niobium–tantalum oxide obtained was calcined at 800 °C for 1 h giving a (Nb,Ta)2O5 product (99.3%) containing Fe2O3 0.08%, TiO2 0.05%, SiO2 0.05% and SnO2 0.01%. Manganese was not detected in the product. Thus impurities in the leach solution could be almost completely separated from the niobium and tantalum, to provide a high purity (Nb,Ta)2O5 product.

Although the impurities (Si, Sn, Ti, Fe, Sn, Mn) in the leach solution showed no effect on the product quality of (Nb,Ta)2O5, they may cause a negative effect on the recycling of excess KOH. Therefore, an impurities removal procedure is introduced in this new improved process (Fig. 1). We have not yet done a systematic study on the impurities removal, but the method developed by our research group for the separation of silica from KOH solution through addition of CaO (Wang et al., 2008) can be adopted. Through this method, the silica will be removed from the KOH solution in form of 1.5CaO·SiO2·H2O precipitate. Meanwhile, Sn and Ti will also be removed in the form of CaSnO3 and CaTiO3 precipitates. Iron and manganese in the KOH solution are mainly in forms of KFeO2 and KMnO2. We found that Fe and Mn concentrations in the KOH solution decreased significantly after the solution was left for a period, which was presumably attributable to the hydrolysis of KFeO2 and KMnO2. Therefore, the hydrolysis of KFeO2 and KMnO2 through heating the KOH solution is an effective way for the removal of Fe and Mn. The impurities removal procedure is important and has become the focus of our research which will be reported later.

4. Conclusions

(1) A new improved method is proposed for the leaching of low-grade niobium–tantalum ores, which includes ore enrichment with Nb2O5, KOH roasting and decomposition, and water leaching. This method offers higher recoveries of Nb and Ta than the current HF process.

(2) Enrichment with Nb2O5 favours the formation of water soluble K3(Nb,Ta)O4 and minimizes the formation of insoluble KTaO4 and K(Ta,Nb)O3 in the KOH roast.

(3) The optimum process conditions were determined to be: Nb2O5-to-Ta2O5 mass ratio 2.33:1; KOH decomposition temperature 400 °C; KOH-to-ore mass ratio 2:1; decomposition time 60 min. Under these conditions, the leach recovery of niobium and tantalum was about 94.7% and 93.6% respectively. About 80% Si and Sn, 50% Ti and <20% Fe and Mn were also leached.

(4) High purity (Nb,Ta)2O5 (99.3%) was obtained from the leach solution through evaporation/crystallization/phase transformation with dilute acid and calcination.

(5) Compared with the sub-molten salt method proposed earlier, the KOH-to-ore mass ratio decreased from 7:1 to 2:1 resulting in reduced energy consumption.

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Table 2

<table>
<thead>
<tr>
<th>Leaching time/min</th>
<th>Elements leached/%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nb Ta Fe Mn Sn Ti Si</td>
</tr>
<tr>
<td>60</td>
<td>95.07 92.99 9.06 19.60 80.66 51.29 76.57</td>
</tr>
<tr>
<td>120</td>
<td>95.33 93.22 8.88 17.59 81.34 54.26 74.40</td>
</tr>
<tr>
<td>180</td>
<td>96.19 93.01 10.52 21.45 80.01 60.63 65.05</td>
</tr>
</tbody>
</table>

(Mass ratio of Nb2O5-to-Ta2O5 2.33:1, 400 °C, mass ratio of KOH-to-ore 2:1.)
(6) From a process point of view, the Nb₂O₅ used for enriching the niobium–tantalum ore can be recycled from some of primary Nb₂O₅ product or realized by mixing with another ore in which the Nb₂O₅-to-Ta₂O₅ mass ratio is high.

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References


