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Niobium Oxide and Tantalum Oxide Micro- and Nanostructures Grown Using Material Recovered from Mining Tailing

B. Sotillo [1], L. Alcaraz [2,*], F. A. López [2], F. J. Alguacil [2], O. Rodríguez [2], and P. Fernández [1]

[1] Department of Materials Physics, Faculty of Physics, Complutense University of Madrid, Madrid, Spain; bsotillo@fis.ucm.es (B.S.); arana@fis.ucm.es (P.F.)

[2] National Center for Metallurgical Research (CENIM), Spanish National Research Council (CSIC), Avda. Gregorio del Amo 8, 28040 Madrid, Spain; alcaraz@cenim.csic.es (L.A.); f.lopez@csic.es (F.A.L.); fjalgua@cenim.csic.es (F.J.A.); olga.rodriguez@csic.es (O.R.)

* Correspondence: alcaraz@cenim.csic.es

Abstract: Niobium and tantalum based oxides were recovered from mining tailing. These oxides were used as starting material for growing micro- and nanostructures by an evaporation method. Morphology and crystal structure of the final oxides were evaluated using X-ray diffraction (XRD), micro-Raman spectroscopy, and scanning electron microscopy (SEM). After the thermal treatment, microrods of both oxides were obtained, presenting exotic stoichiometries: $Nb_{22}O_{54}$ and $K_6Ta_{10.8}O_{30}$, respectively.

Keywords: metals recovery; strategic metals; microstructures grown, mining tailing, niobium oxide, tantalum oxide

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1. Introduction

Two main problems faced by the increasingly technological society are the huge amount of waste that humans generate and the scarcity of many of the materials used. In this sense, one of the EU's priorities is to promote the transition to a circular economy, where the materials and products manufactured with them are kept in the life cycle as long as possible. Nb and Ta are highly appreciated metals due to the several technological applications in high-strength alloys, capacitors, supercapacitors [1], catalysis [2], coatings or light guiding [3], electrochemical energy storage devices [4] [5], among others. However, the most important problem is that they are scarcely found in the Earth's crust as raw materials. It is then an interesting topic for the scientific community, to develop new technologies to assure a sustainable use of these raw materials, as well as to improve the processes to recover and recycle them. Due to their importance for high-tech products and emerging innovations, niobium (Nb) and tantalum (Ta) are included in the 2020-year list of the 30 critical raw materials of the European Union [6].

Both Nb and Ta are found as columbotantalite mineral in nature. This mineral can be extracted from mining tailings [7,8], as in the case of Sn-Nb-Ta concentrate extracted from the Penouta mine (Galicia, Spain). However, the low concentration of both metals, along with their strong association with cassiterite (SnO_2), and the similar physical and chemical properties of Nb and Ta, foster the development of tailored procedures to extract and separate them.

In the present work, powders of these two strategic metals oxides, niobium and tantalum, are recovered from the tailings of the Penouta Sn-Ta-Nb deposit (located in Galicia, Spain) via hydrometallurgical route [7,8]. The recovered oxide powders were used to obtain micro- and nanostructures by a thermal evaporation method. The structures have been characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), and micro-Raman spectroscopy. It is shown that the rods grown from the mine-recovered oxide powders have exotic stoichiometries ($Nb_{22}O_{54}$ and $K_6Ta_{10.8}O_{30}$, respectively), rarely studied in the literature.

2. Materials and Methods

The starting material (cassiterite and columbotantalite) was recovered from mining deposits of the Penouta mine (Galicia, Spain). Initially, mining tailings were treated by a pyrometallurgical process in order to obtain a metal tin ingot and a vitreous slag, as previously reported [7,8]. The slag was milled, and leached using a HF/H_2SO_4 mixed during 1 hour. After then, the acid mixture was filtered, and the extraction of the strategic metals was performed. For this purpose, the leaching liquid phase was put in contact with a mixed of 35% (v/v) Cyanex 923® diluted in Solvesso, where niobium and tantalum were extracted into the organic phase with yields at around 98%. Then, this organic phase was treated to carry out a selective separation of both strategic metals: first, it was stripped with NH_4F/NH_3 (0.27M/0.106M) where niobium was extracted to the aqueous phase; subsequently, a NH_4F/NH_3 (1.08M/0.42M) was added to the secondary organic phase, and the tantalum in the aqueous phase was recovered [7,8]. Once the Nb and Ta were separated, the corresponding aqueous solutions were precipitated using NH_3 (concentrate, 17.7M) and KF (90 g/L), respectively. After this process, hydrated Nb oxide ($Nb_2O_5 \cdot nH_2O$) and $K_{0.4}Ta_{2.4}F_{0.6}$ compounds were collected. In order to reach the corresponding solid oxide precursors, both Nb and Ta precipitates were calcinated in a tubular furnace at 1200 °C. The procedure to obtain the different samples is shown in Figure 1. Further details of this process can be found in [8].

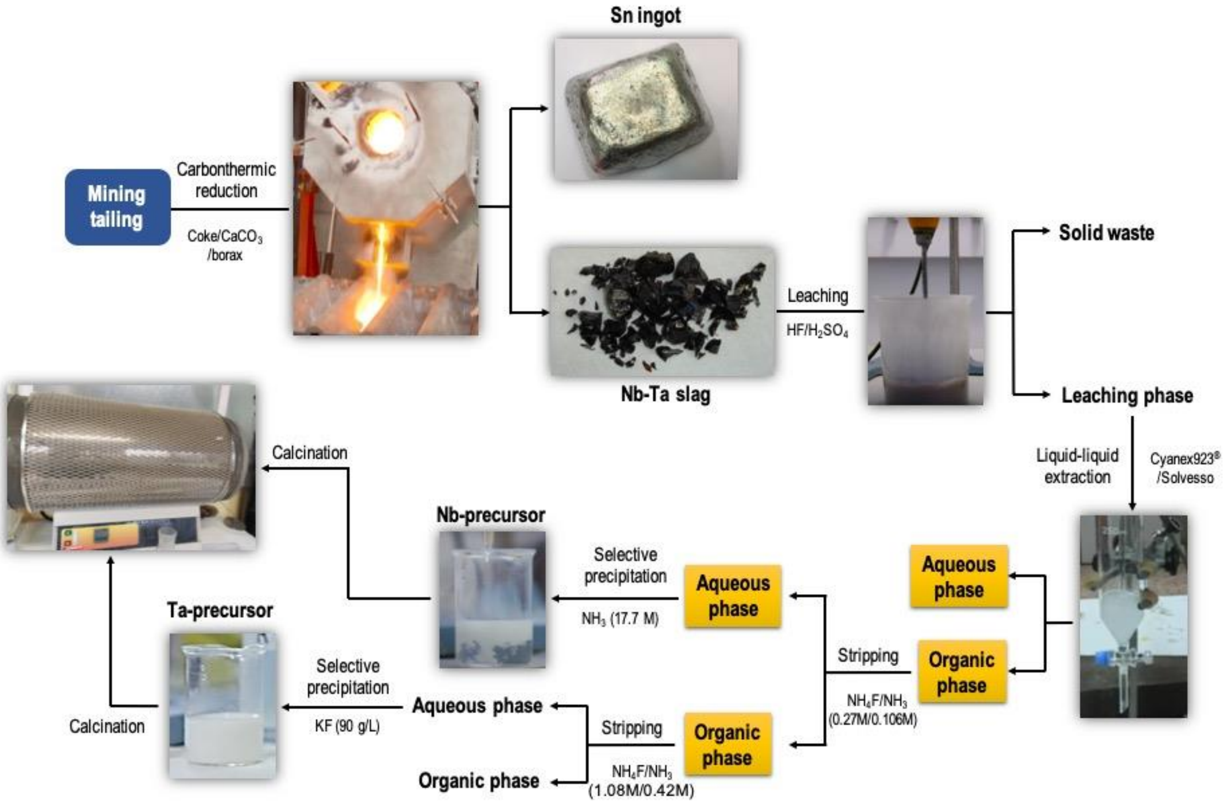

Figure 1. Schematic procedure realized to obtain the corresponding niobium and tantalum precursor oxides.

Once niobium and tantalum oxide powders were recovered, were used to grow microstructures. The powders were placed on an alumina boat and inside a furnace. Then, the powders were subjected to a thermal treatment, with different conditions depending on the precursor. For niobium oxide, the best conditions to grow microstructures were

1300°C during 10h with an Ar flux. On the other hand, for the tantalum oxide, the treatment to obtain the microstructures were: 1500 °C during 8 h under a continuous Ar flux.

The morphology of the recovered powders and of the grown microstructures was studied using two scamming electron microscopes: a FEI Inspect and a Hitachi TM3000 SEM. The structural characterization was carried out through X-ray diffraction (XRD) and micro-Raman spectroscopy (μ-Raman). XRD measurements were done in a PANalytical Empyrean diffractometer (Cu-K$_\alpha$ radiation). For performing the μ-Raman measurements, a confocal microscope Horiba JobinYvon LABRAM-HR was employed. The excitation wavelength was 632.8 nm, coming for a He-Ne laser. The laser was focused onto the sample with a 100× Olympus objective, and the scattered light was also collected using the same objective (backscattering configuration). Further details of the characterization can be found in [8–10].

3. Results and Discussion

3.1. Scanning electron microscopy (SEM)

The morphology of the recovered oxide powders (as obtained after the procedure shown in figure 1), is shown in the SEM images of figure 2a,b. As can be appreciated, irregular shaped particles were obtained in both cases after the recovery process. Just in the case of tantalum oxide, some rod-type particles can be identified (figure 2b). It is only after the thermal treatments when a high density of microrods are observed. They typically have rectangular sections, as shown in the corresponding SEM micrographs in figure 2c,d.

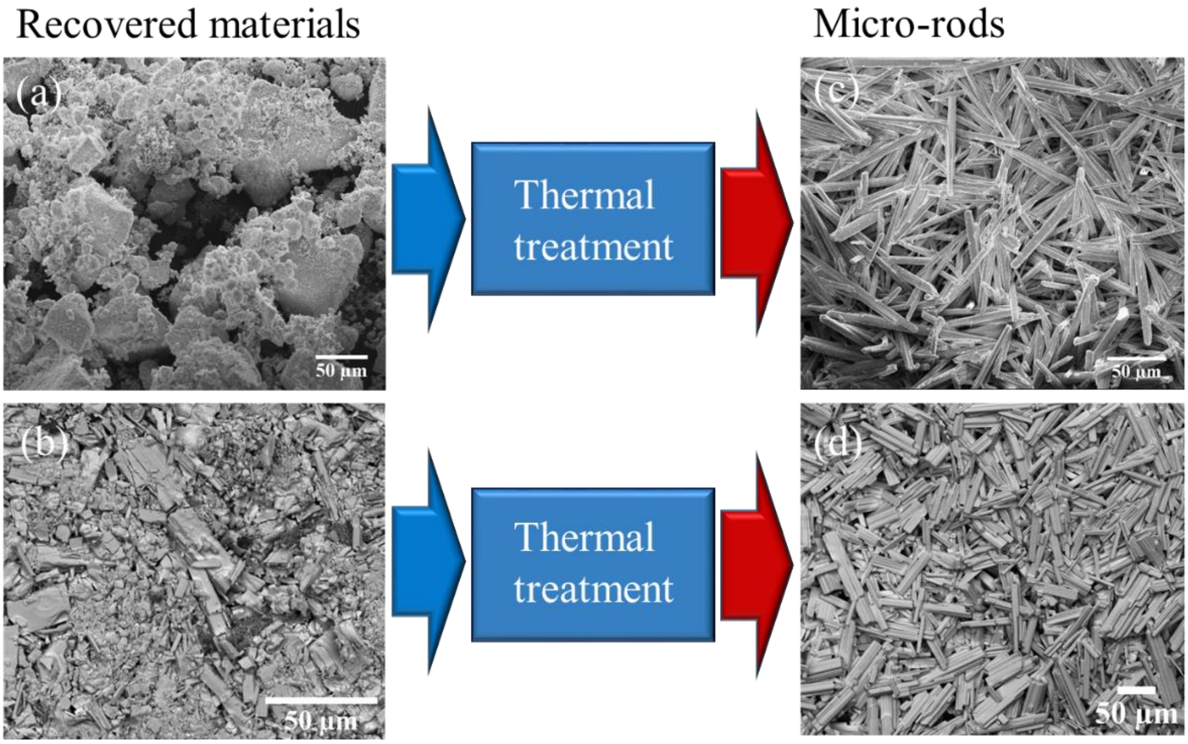

Figure 2. SEM micrographs of the niobium and tantalum compounds: (a) SEM of the niobium oxide powders and (b) tantalum based oxide powders recovered after the procedure indicated in figure 1. After a thermal treatment of the recovered materials in Ar flux microrods are obtained: (c) SEM image of niobium oxide and (d) tantalum based oxide rods.

3.2. X-ray diffraction (XRD)

Upon the thermal treatment, a phase transformation was observed in niobium oxide. The powders recovered after the process shown in figure 1 were mainly in the pseudo-hexagonal phase (TT) of Nb_2O_5 (figure 3a, inset). The most intense reflection was indexed to this phase (ICDD nº. 00-028-0317). Some less intense peaks can be ascribed to a $Nb_{12}O_{29}$ non-stoichiometric monoclinic phase (ICDD nº. 04-014-6587) and quartz impurities, but the results indicate that was possible to recover niobium oxide compounds. After the thermal treatment at 1300°C, the main phase registered is $Nb_{22}O_{54}$ (monoclinic phase, ICDD nº. 04-014-9203). This information was extracted from the XRD pattern shown in figure 3a.

On the other hand, no phase transformation is produced in the tantalum oxide material during the thermal treatment. The most intense reflection maxima in the XRD pattern (figure 3b, inset) can be indexed to the tetragonal tungsten bronze-like structure of $K_6Ta_{10.8}O_{30}$ (ICDD nº. 01-070-1080). This results indicated that the procedure was not able to remove the possatium from the crystal structure of the recovered material. The XRD pattern after the treatment at 1500°C (figure 3b) exhibited diffraction maxima according to the same $K_6Ta_{10.8}O_{30}$ tetragonal tungsten bronze-like structure. This result reveals that this material does not transform its crystal phase as previously described in [8].

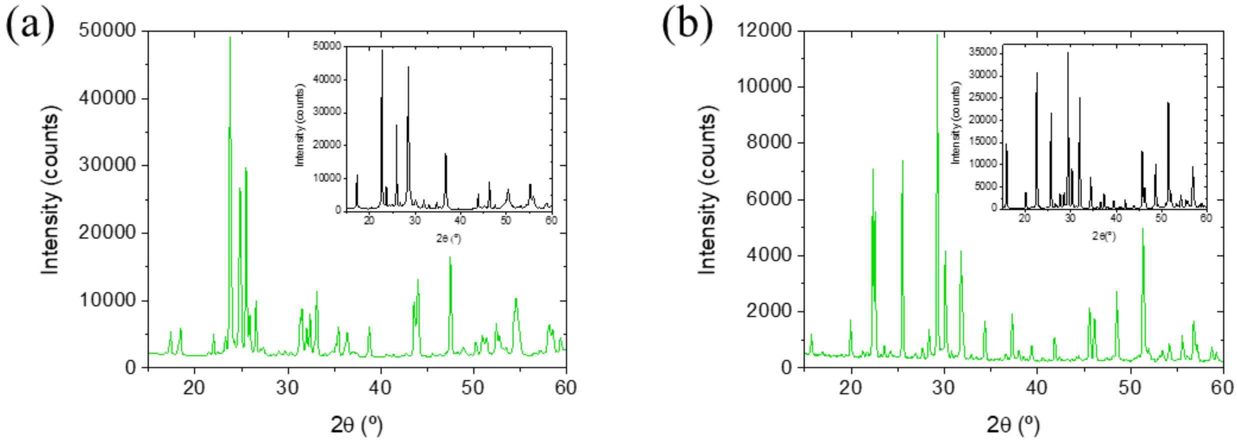

Figure 3. Comparative of the XRD patterns taken on the rods of (a) niobium oxides; (b) tantalum based oxides. In the insets, the XRD of the initial recovered materials are shown. .

The crystal structures obtained in this work may be useful in the fabrication of energy storage devices, as they have crystallographic channels or tunnels where the insertion of ions is possible without producing a large alteration of the volume [11]. Also, the obtained rods shown a high value of refractive index [9,10], as expected for these oxides.

3.3.μ-. Raman spectroscopy

Further studies of the crystal structure of the niobium and tantalum oxides were performed using μ-Raman spectroscopy (Figure 4). For both niobium and tantalum oxides, the crystal structures can be seen as a weave of corner-linked XO_6 octahedra (being X= Nb or Ta). Most of the observed bands in the Raman spectra can be related to the internal modes of XO_6 polyhedra [12,13]. The $200\ cm^{-1} < \nu < 450\ cm^{-1}$ region would correspond to the bending related modes of the XO_6 octahedra; while in the $450\ cm^{-1} < \nu < 900\ cm^{-1}$ region the modes related to the stretching vibrations of the X-O bonds in the XO_6 octahedra will be found. Typically, the external lattice vibrations (for which the octahedra is considered as a rigid unit) are found at $\nu < 200\ cm^{-1}$. The sharp mode observed at $520\ cm^{-1}$ corresponds to the silicon substrate.

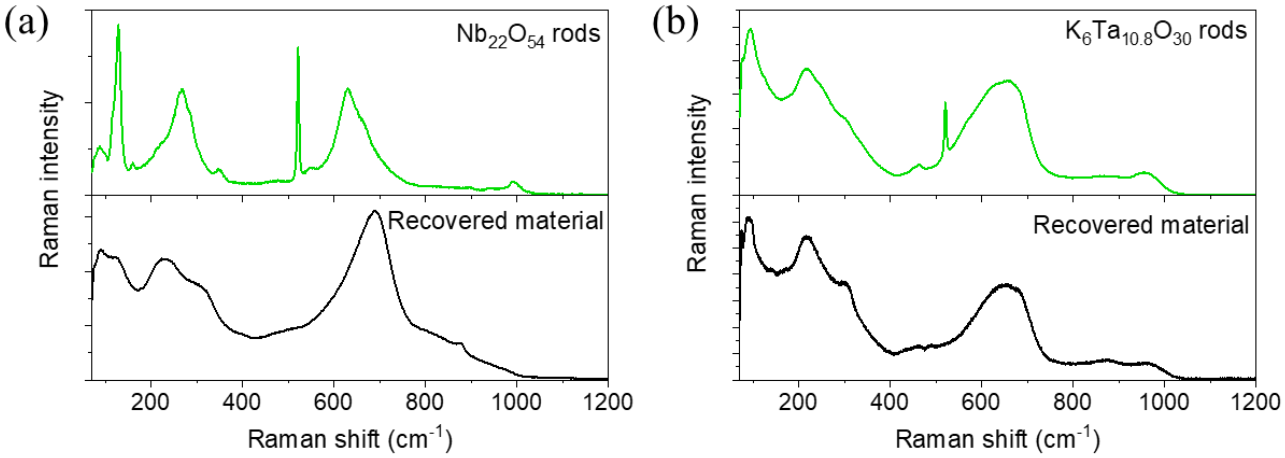

Figure 4. µ-Raman spectra recorded on the recovered materials as well as on the microrods: (a) niobium oxide; (b) $K_6Ta_{10.8}O_{30}$.

In the case of niobium oxide material (Figure 4a), differences between the recovered material and the rods are detected in the Raman spectra. The bands observed in the recovered material are the expected for the TT-Nb_2O_5 phase. On the other hand, the rods present modes that are associated with monoclinic phases (as it is the $Nb_{22}O_{54}$ compound). The displacement of the band at around 690 cm^{-1} towards lower wavenumber indicates an increasing bond order of octahedra and a more ordered crystal structure. In addition, some of the peaks are sharper than in the recovered material, in agreement with this increase in the crystal order. The new band at 993 cm^{-1} is associated to the symmetric stretching modes of the terminal bonds of Nb=O in NbO_6 octahedra.

As expected, it the case of $K_6Ta_{10.8}O_{30}$ material (Figure 4b), no strong changes are observed between the recovered powders and the rods, as no phase transformation was produced.

A detailed description of the physical properties of the obtained microrods for both materials can be found in [10] ($Nb_{22}O_{54}$) and in [9] ($K_6Ta_{10.8}O_{30}$).

4. Conclusions

In the present work, a process to obtain micro- and nanostructures of niobium and tantalum oxides from mining tailing is described. Pyrometallurgical treatment, followed by a selective liquid-liquid extraction and a subsequent precipitation were used to obtain Nb and Ta precursors. These solids precursors were treated in a furnace under Ar flux to grow the corresponding structures.

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Conflicts of Interest: The authors declare no conflict of interest.

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