

Modifying the Physicochemical and Electrical Properties of Tantalite and Columbite Surfaces under Conditions of Electrochemical Treatment and High-Voltage Nanosecond Pulses

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Abstract—Structural and chemical modifications of tantalite and columbite surfaces, induced by treating the minerals with anolyte—a product derived via the electrolysis of aqueous solutions—and high-voltage electromagnetic pulses, are studied by means of X-ray photoelectron spectroscopy, scanning electron microscopy, energy-dispersive spectroscopy, atomic force microscopy, and electrophoretic light scattering. The mechanical properties of the surfaces are characterized via Vickers microhardness testing. Treating the minerals with anolyte removes iron-containing surface films and leads to considerable conversion of surface-confined Fe(II) species into Fe(III), increasing the differences between the physicochemical and electrical properties of these rare earth minerals. The nonthermal impact of high-voltage pulses results in effective surface softening, a reduction in microhardness, and the disintegration of mineral particles, yielding surface micro- and nanosized phases enriched with iron and oxygen.

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INTRODUCTION

Due to the structural texture properties, fine embedded structure, and intergrowth characteristic of ores of rare earth metals, the enriching of niobio–tantalate ores to obtain commercial concentrates suitable for further chemical and metallurgical processing remains an unsolved problem. The low efficiency of flotation extraction for selective columbo–tantalite concentrates can be attributed to iron oxide and hydroxide on the surfaces of the minerals to be separated, which effectively eliminates the differences (important in flotation) between their physicochemical and sorption properties [1].

In this work, we investigate mechanisms of the deliberate surface modification of such rare earth–metal minerals as tantalite and columbite with acidic anolyte ($\text{pH} < 5$)—a product of the electrolysis of an aqueous solution [2]—and high-voltage nanosecond pulses (HVNP) [3–6]. We do this to differentiate between the physicochemical and structure-sensitive surface properties (e.g., microhardness and surface electric potential) of the abovementioned minerals.

Columbite and tantalite, which are complex oxides with the general formula $A_m B_n X_p$ (AB_2X_6), are n -type semiconductors with low surface conductivities of 4.0×10^{-7} and 6.5×10^{-7} S cm^{-1} , respectively [7, 8].

Their respective Seebeck coefficients are 150 and 20 $\mu\text{V K}^{-1}$ [8, 9].

EXPERIMENTAL

The tantalite we used contained small amounts of Ti^{4+} and Sn^{4+} admixtures and was essentially a manganese-containing niobio–tantalite mineral with the formula $(\text{Mn}_{0.80}\text{Fe}_{0.15}^{2+}\text{Fe}_{0.05}^{3+})_{1.00}(\text{Ta}_{1.15}\text{Nb}_{0.80}\text{Ti}_{0.03}\text{Sn}_{0.02})_{2.00}\text{O}_{6.00}$ (stoichiometric formula, (Fe, Mn)(Ta, Nb) $_2\text{O}_6$). The columbite with the formula $(\text{Mn}_{0.91}\text{Fe}_{0.08}^{2+}\text{Fe}_{0.01}^{3+})_{1.00}(\text{Nb}_{1.79}\text{Ta}_{0.20}\text{Ti}_{0.01})_{2.00}\text{O}_{6.00}$ (stoichiometric formula, (Fe, Mn)(Nb, Ta) $_2\text{O}_6$) was in granular form with grain sizes of $(-3 + 0.5)$ mm. The chemical composition, morphology, and crystallographic properties of these minerals were studied in [10].

Samples of the minerals were treated for 1 hour in anolyte with $\text{pH} = 3.5\text{--}3.7$, $E_h = 800\text{--}900$ mV, and a dissolved oxygen concentration of ~ 24 mg/L. Anolyte, which can serve as a potent oxidizer in mineral leaching [2], was prepared via the electrolysis of water in a diaphragm electrolyzer with a ruthenium oxide-coated anode at volume current density $I_v = 0.4\text{--}0.6$ A/L for 25 min. Reference treatments were performed using an HCl solution with $\text{pH} = 3\text{--}3.5$ for 3 h. (This solution is employed in familiar protocols for preparing

columbo–tantalite gravity concentrates for flotation extraction [1].)

The minerals under study were subjected to the non-thermal effects of HVNPs with rising times of 1–5 ns, pulse lengths of ~50 ns, amplitude voltages of ~25 kV ($E \sim 10^7$ V/m), pulse repetition frequency of 100 Hz, and pulse energies of ~0.1 J. Length of exposure t_{exp} varied between 10 and 100 s; i.e., number N_p of HVNPs was $(1-10) \times 10^3$. Treatment was performed in the ambient environment under standard conditions, with mineral particles in contact with the grounded pulse generator electrode. This sometimes resulted in sparking between the mineral particles and the active electrode (anode) surface [11].

The chemical states of atoms on the tantalite and columbite surfaces were analyzed via X-ray photoelectron spectroscopy (XPS) on a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K_{α} X-ray source ($E_{\text{photon}} = 1486.6$ eV) operating at an emission current of 20 mA and a tube filament voltage of 10 kV. The chamber pressure was held at 10^{-8} Pa or less. XPS spectra were recorded in the fixed analyzer transmission (FAT) mode, with a transmission energy of 160 eV for recording survey spectra and 40 eV for measuring the bonding energy of the electron states of key elements Nb 3d, Ta 4f, Fe 2p, and Mn 2p. The survey spectra were recorded with steps of 1 eV; for individual lines, the step was set at 0.05 eV. Details of the practical aspects of XPS analysis of minerals can be found in [10, 12, 13].

The chemical composition and morphology of mineral samples were analyzed via scanning electron microscopy (SEM) on a LEO 1420VP electron microscope equipped with an INCA 350 EDS system (Oxford Instruments) for energy dispersive X-ray analysis. Electric surface potentials and additional topographical data were acquired with a Ntegra Prima atomic force microscope (AFM) manufactured by NT-MDT (Zelenograd).

The effectiveness of treating the investigated mineral particles with anolyte, HCl solution, and HVNPs was assessed from changes in the electrical properties of the minerals (open circuit potential (OCP) ϕ , V; electrokinetic potential ζ , V; and electrostatic surface potential V_s , V) and their microhardness (according to Vickers HV , MPa). The amounts of Fe and Mn leached from the minerals into the liquid phase were determined by chemical means and atomic absorption spectroscopy [10].

The OCPs for our columbite and tantalite samples was determined via potentiometric titration while simultaneously recording a solution's pH. The potential was measured against a saturated Ag/AgCl electrode. The ζ -potentials of mineral particles <10 μm in size in distilled water, anolyte, and HCl were measured via electrophoretic light scattering on a Zetasizer

Nano ZS universal particle analyzer (Malvern Instruments).

Kelvin probe force microscopy (KPFM) was used to measure the electrostatic potential on the surfaces of cleaved tantalite samples attached to a grounded support [14], using NSG10/TiN probes with a conducting TiN coating, a stiffness constant of 11.8 N/m, and a tip radius of 35 nm. The resonant frequency was set at ~260 kHz. Sample topography was imaged during the first scan, and the z -component of the surface electrostatic potential was recorded during the second scan, maintaining an approximately 5–10 nm distance of separation between the tip and the surface being imaged.

Vickers microhardness testing for columbite and tantalite samples before and after treatment with anolyte and HCl was performed in accordance with GOST-2999-75 on a PMT-3M microhardness tester with a load of 100 g and loading times of 10–15 s, respectively.

RESULTS AND DISCUSSION

XPS analysis showed that the chemical state of Nb and Ta atoms in the surfaces of the minerals treated with anolyte and HCl solution went essentially unchanged. The main effect treatment with these acidic solutions had on the valence state of surface atoms was the oxidation of surface Fe(II) to Fe(III) species (Table 1). Following treatment with the anolyte, the Fe(III) content in the tantalite sample rose by 29.5 at %, with the dominant species being Fe(III)–OH. For the same mineral, treatment with the HCl raised the total Fe(III)–O and Fe(III)–OH contents to 10.7 at %.

Hydrochloric acid had a minor effect on the columbite surface Fe(III) content, while anolyte induced considerable oxidation of Fe(II) to Fe(III): nearly all surface iron was in a trivalent state (96.6 at %), with the fraction of Fe(III)–OH species at a level of 64.2 at % (Table 1). Along with surface iron species, treating the columbite with anolyte and HCl increased the surface Mn(II) concentrations with a concomitant drop in surface Mn(IV) concentrations, due presumably to the reduction of the latter to the former.

With the observed changes in the physicochemical properties and chemical composition of the liquid phase in which the mineral particles were suspended, the use of anolyte resulted on average in a 1.2–1.5 increase in iron and manganese concentrations, compared to HCl treatment [10]. For columbite, anolyte treatment resulted in an Fe(III) concentration of 6.3×10^{-8} mg cm^{-3} , 8.6 times higher than the one after HCl treatment (0.73×10^{-8} mg cm^{-3}) [10].

The OCPs of the columbite and tantalite shifted anodically after treatment in the described liquids, with anolyte producing a total shift of 200–250 mV into the area of positive values for columbite, in con-

Table 1. Changes in the chemical state of tantal, niobium, iron, and manganese atoms in the surfaces of tantalite and columbite specimens treated with anolyte or HCl solution, according to XPS data

| Mineral | XPS peak | Bonding energy, eV | Attributed to | Before treatment | After treatment with anolyte | After treatment with HCl |
|-----------|----------|--------------------|--------------------------------|------------------|------------------------------|--------------------------|
| | | | | at % | | |
| Tantalite | Ta 4f | 26.0 | Ta ₂ O ₅ | 54.9 | 56.8 | 55.9 |
| | | 27.9 | | 45.1 | 43.2 | 44.1 |
| | Nb 3d | 206.9 | Nb ₂ O ₅ | 58.7 | 60.6 | 58.1 |
| | | 208.9 | | 41.3 | 39.4 | 41.9 |
| | Fe 2p | 709.5 | Fe(II)–O | 34.4 | 5.0 | 23.8 |
| | | 711.2 | Fe(III)–O | 52.3 | 36.7 | 58.3 |
| 713.2 | | Fe(III)–OH | 13.2 | 58.4 | 18.0 | |
| Columbite | Nb 3d | 207.1 | Nb ₂ O ₅ | 60.5 | 60.2 | 60.8 |
| | | 209.9 | | 39.5 | 39.8 | 39.2 |
| | Fe 2p | 709.5 | Fe(II)–O | 19.7 | 3.5 | 17.6 |
| | | 711.2 | Fe(III)–O | 52.1 | 32.4 | 56.3 |
| | | 713.2 | Fe(III)–OH | 28.2 | 64.2 | 25.8 |
| | Mn 2p | 640.2 | Mn(II) MnO | 57.0 | 60.5 | 65.8 |
| | | 641.1 | | | | |
| | | 641.9 | Mn(IV) MnO ₂ | 43.0 | 39.5 | 34.2 |
| 642.7 | | | | | | |

Table 2. Changes in the OCP, ζ -potential, electrostatic potential (V), and microhardness (HV) for tantalite and columbite samples after processing with anolyte, HCl solution, or HVNPs

| Mineral | OCP, mV (pH 3.5) | | ζ -potential, mV | | V , mV | | HV , MPa | | | | |
|-----------|------------------|-----|------------------------|---------|----------|-------|------------|------|---------|-------|-----------------------------------|
| | Treatment | | | | | | | | | | |
| | anolyte | HCl | none | anolyte | HCl | none | anolyte | none | anolyte | HCl | HVNPs $t_{\text{exp}} = 100$ s |
| Tantalite | 190 | 140 | –22.4 | 3.1 | 1.6 | –16.9 | –39.4 | 984 | 757.5 | 893 | 784 |
| Columbite | 460 | 270 | –24.8 | 2.4 | 9.4 | – | – | 953 | 726 | 796.4 | – |

trast to the HCl solution; under the same conditions, the shift in the tantalite's OCP was 20–80 mV into the area of positive values, in agreement with the XPS data (Table 2).

The columbite and tantalite surfaces consisted of positively charged Fe(II) and Mn(II) species, along with phases of hydrated iron oxides. The ζ -potential of suspended mineral particles was due to the transfer of ionic species from the particles' surfaces into the phase of the solution, resulting in a build-up of surface charge; near-surface iron and manganese cations are thus potential-determining ions for columbite and tantalite, while negatively charged hydroxyl ions (from the phase of the solution) act as counter-ions, thus determining the negative ζ -potential of these minerals at neutral pH (Table 2).

The intense consumption of oxygen by the surfaces of mineral particles was observed during treatment with anolyte, due to the oxidation of the iron(II) species: $\text{Fe(II)} - e^- \rightarrow \text{Fe(III)}$. Other observed phenomena were the dissolution of surface hydroxide films and the leaching of Fe(II) and Mn(II) from the surface layer of the columbite, upsetting the surface's electroneutrality. This led to the buildup of a negative charge on the mineral's surface (the liquid phase anions) and an excess positive charge, due to hydronium ions in the adjacent solution layer. In other words, an electrical double layer with a positive diffuse part formed at the solution/mineral particle interface, producing a positive ζ -potential (Table 2).

The electrostatic potential of the tantalite surface was found to be negative (with respect to the tip poten-

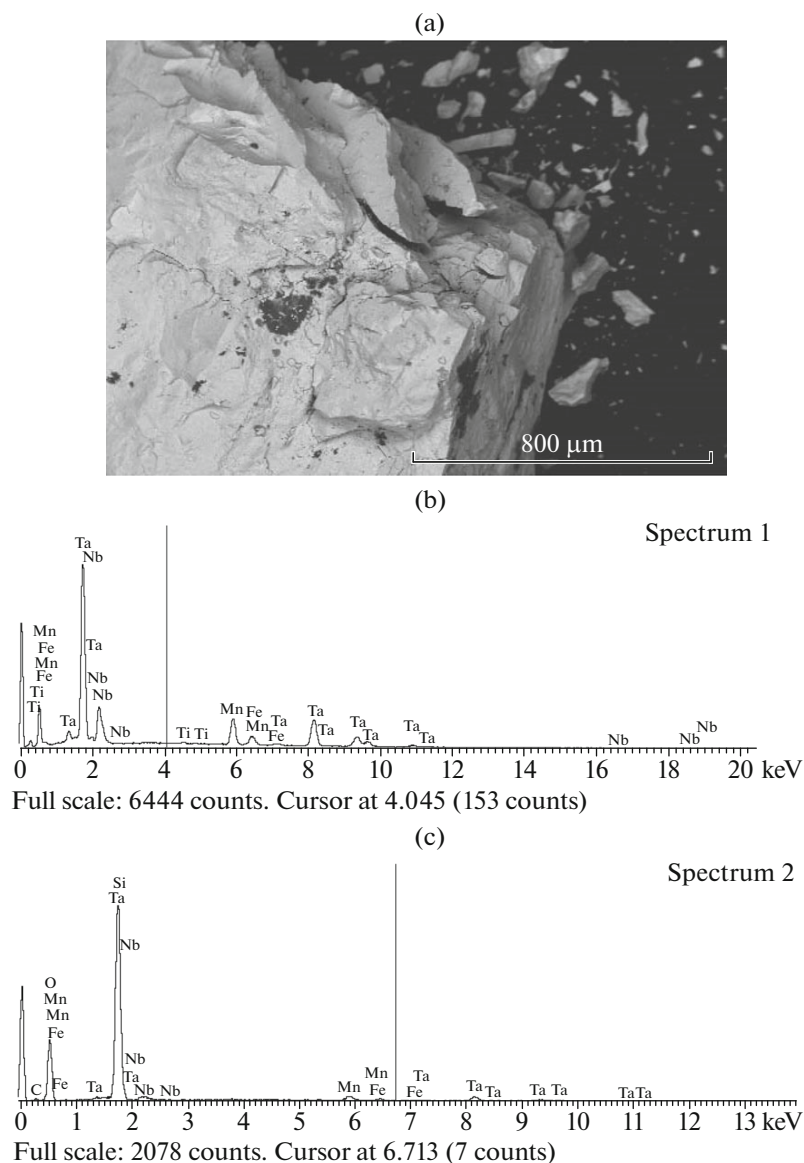


Fig. 1. (a) SEM image of a tantalite particle after exposure to HVNPs ($t_{\text{exp}} \sim 10$ s) and (b, c) EDS spectra sampled from two different points of the mineral surface (scale bar is 800 μm).

tial), as was indicated by the KPFM measurements (Table 2). Following treatment with anolyte, the potential shifted by 18–22 mV into the area of negative values, due to the partial leaching of Fe(II) cations off the mineral surface, resulting in a negative charge on the surface of the mineral that was not compensated for.

SEM imaging and elemental mapping with EDS revealed the presence of microcracks and scattered particles (as a result of the disintegration of material) on the surfaces of the minerals (Fig. 1). Micro- and nanoscopic surface phases with different morphologies (Fig. 2) were seen on the tantalite's surface; these were chemical and structural modifications resulting from nonthermal treatment with HVNPs.

EDS elemental mapping showed that the particles formed on the tantalite surface were slightly enriched with iron and oxygen, while their manganese content was reduced (Fig. 2a). The low contrast between these particles and the background surface in the SEM images acquired in the backscattered electron mode suggests only slight compositional differences. At the same time, the high contrast for Nb and O does not reflect the true distribution of these elements; rather, it is a result of the complicated topography of the sample.

The contrast in the SEM image of a fairly smooth region of the surface (Fig. 2b) correlates with the distribution of elements. For example, elevated levels of

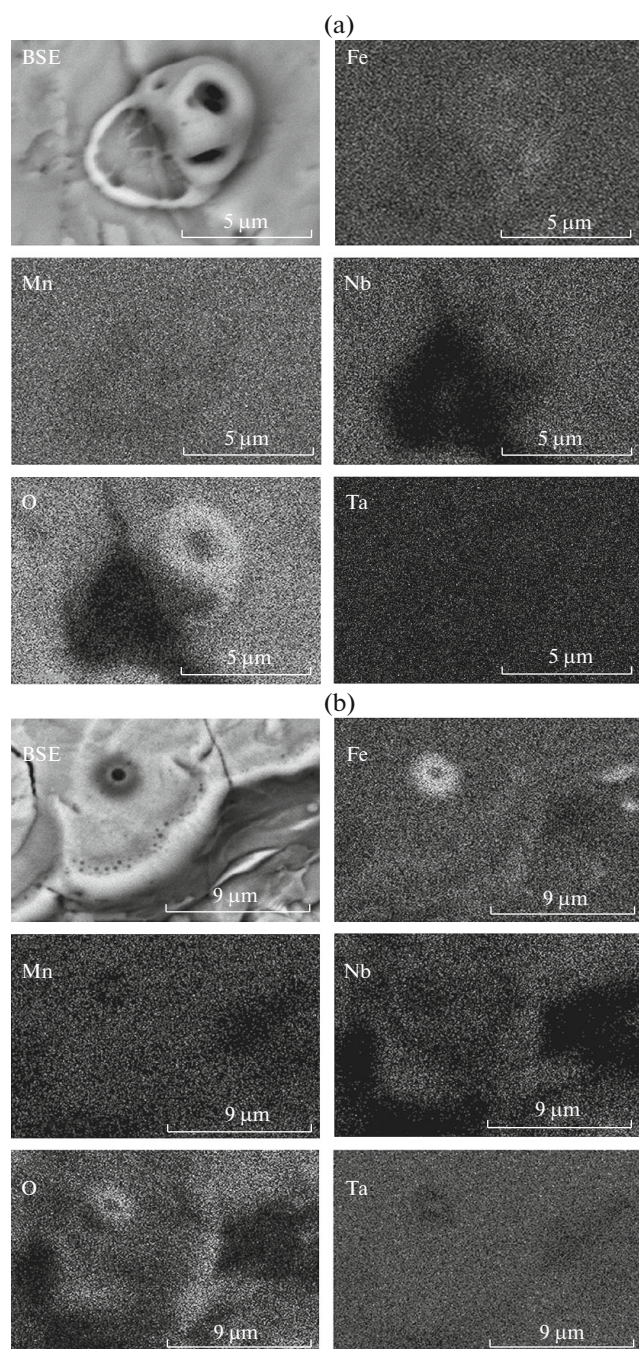


Fig. 2. SEM (back-scattered electron) images of the topography of two particles (a and b) formed on a tantalite surface after exposure to HVNPs ($t_{\text{exp}} \sim 50$ s) and EDS element mapping for Fe, Mn, Nb, O, and Ta in the same region. Scale bars are (a) 5 μm and (b) 9 μm.

Fe and O and a reduction in Mn, Nb, and Ta are observed in the dark area along the edges of the trench containing elements lighter on average than the rest of the surface. The phase along the wave-like edge of the sample's flaking (Fig. 2b) appears with low contrast in the SEM image and likely had an elemental composition similar to the new particles shown in Fig. 2a.

Within this region, the iron and oxygen contents are elevated only slightly, while the concentrations of other elements exhibit minor fluctuations.

The chemical and structural modifications of the surfaces of the investigated minerals, produced by treating them with acidic solutions and exposing them to the nonthermal effects of HVNPs, were effective in softening their surfaces (Table 2). The relative reduction in microhardness ΔHV of the tantalite samples (Mohs hardness, 5.5–6) following treatment with anolyte, HCl solution, and HVNPs, was 23, 9.2, and 20.3%, respectively. These values were calculated using the equation $\Delta HV = (HV_{0i} - HV_i) / HV_{0i}$, where HV_{0i} and HV_i are the microhardness of the i -th sample before and after treatment.

Treating the columbite (Mohs hardness, 6–6.5) with HCl solution reduced its microhardness from 953 to 796.4 MPa. With anolyte, it was reduced to 726 MPa (in relative terms, by 16.4 and 23.8%, respectively).

CONCLUSIONS

Treating tantalite and columbite specimens in anolyte rather than HCl solution proved to be more efficient in removing iron-containing films from the minerals' surfaces during the oxidation of surface species of Fe(II) into Fe(III) (which led to their softening) and induced a positive shift in the minerals' electrostatic and electrokinetic (ζ) potentials. High-voltage nanosecond pulses caused the disintegration of mineral particles, resulting in micro- and nanosized surface phases with elevated levels of iron and oxygen, along with a 20–24% drop in the microhardness (ΔHV_{max}) of tantalite.

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