

The Mechanism of Structural and Chemical Transformations of Tantalite, Columbite, and Zircon Surfaces in the Process of Acid and Electrochemical Treatment of Mineral Suspensions

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Received May 23, 2016

Abstract—The results of experimental studies and scientific substantiation of an effect of directional change in the chemical and phase composition of the surface and increase in the contrast of physicochemical and electrical properties of tantalite, columbite, and zircon in the course of treatment with anolyte (pH < 5) and a hydrochloric acid solution (HCl, pH 3–3.5) are reported. The mechanism of structural and chemical transformations of the mineral surface in the process of leaching with acid solutions are studied. This mechanism includes the activation of oxidation of iron atoms in the surface layer of tantalite and columbite with the transition from Fe(II) to Fe(III), destruction of the zircon surface with the formation of oxygen–vacancy defects of the SiO_3^{2-} - and SiO_2^0 -types, and intense dissolution of iron- and silicate-bearing films from the surface of rare-metal minerals.

DOI: 10.1134/S1028334X1704016X

Russian resources of tantalum and niobium mostly occur in endogenic deposits and are contained in poor, potentially commercial ores of an unconventional type [1, 2]. Such ores are characterized by a low concentration of rare metals (0.0*n*–0.*n* wt % Nb_2O_5 in Nb–Ta ores) and by a great diversity of impurities of related elements, such as P, Zr, Fe, Ti, REEs, Sr, Ba, Th (alkaline metasomatic rocks with Ta-bearing pyrochlore and columbite [2]) or Be, Rb, Cs, and Sn (granite and pegmatite).

Obtaining conditioned concentrates suitable for further chemical and metallurgical processing is one of the important, but still unsolved problems in Nb–Ta ore processing, which is explained by the textural and structural ore peculiarities, i.e., fine impregnation and mutual intergrowths of rare-metal minerals. In addition, successful flotation extraction of selective concentrates is complicated and sometimes impossible due to the presence of iron oxide and hydroxide films on the surface of separated minerals, which worsens the physicochemical and sorption properties of the surface. The valence of iron on the mineral surface plays the most important role in floatation with complex-forming sorbents (hydroxamic acids), because the stability constant (log*K*) of trivalent iron

hydroxamate is much higher than that of divalent iron hydroxamate (11.4 and 4.8, respectively [3]).

This study is aimed at understanding the mechanism of directional change in the composition of the surface and of the increase in the contrast of physicochemical and electrical properties of tantalite, columbite, and zircon. We carried out treatment of minerals and mineral suspensions with an acid product of the electrochemical treatment of water (anolyte) with pH < 5, which was characterized by a high oxidizing activity in the processes of leaching and oxidation of the mineral surface [4]. We used a solution of HCl (pH 3–3.5) that is applied in the known techniques of preparation of Ta–Nb gravitational concentrates for the process of floatation in our comparative runs [1, 2].

We studied rare-metal minerals, namely tantalite $(\text{Mn}_{0.80}\text{Fe}_{0.15}^{2+}\text{Fe}_{0.05}^{3+})_{1.00}(\text{Ta}_{1.15}\text{Nb}_{0.80}\text{Ti}_{0.03}\text{Sn}_{0.02})_{2.00}\text{O}_{6.00}$, columbite $(\text{Mn}_{0.91}\text{Fe}_{0.08}^{2+}\text{Fe}_{0.01}^{3+})_{1.00}(\text{Nb}_{1.79}\text{Ta}_{0.20}\text{Ti}_{0.01})_{2.00}\text{O}_{6.00}$ (their chemical composition is free of minor admixtures, wt %: 71.8 Nb, 2.68 Ta, 10.48 Fe_{total} , 8.07 Fe(II), 2.05 Fe(III), 9.22 Mn), and zircon ZrSiO_4 (wt %, 63.88 Zr + Hf, 9.66 Si, 1.08 Fe_{total} , 0.62 Fe(II), and 0.46 Fe(III)) extracted from gravitational concentrates from Russian deposits by the gravitational–magnetic–electric scheme. The method of atomic emission spectroscopy with inductively coupled plasma (Varian Vista CCD Simultaneous ICP-AES) was used for analysis of the bulk concentration of elements in the mineral samples studied.

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Finely dispersed mineral samples were treated with anolyte (pH 3.5–3.7, Eh 800–950 mV, concentration of dissolved oxygen ~24 mg/l) and with a HCl solution for 1 h; then the liquid phase was decanted and analyzed for the concentration of Fe, Mn, and Si ions by the chemical and atomic absorption methods.

To analyze the phase composition of the surface of particles of rare-metal minerals, we applied the method of X-ray photoelectron spectroscopy (XPES, Kratos Axis Ultra DLD spectrometer with a monochromatic AlK_{α} source of radiation). XPES was obtained in the mode of constant energy of analyzer transmission, which was 160 eV during registration of panoramic spectra and 40 eV during registration of spectra for internal electron levels of the basic elements: Nb 3*d*, Ta 4*f*, Zr 3*d*, Fe 2*p*, Mn 2*p*, O 1*s*, and Si 2*p*. The panoramic spectrum was recorded with a step of 1 eV; the spectra of individual lines, with a step of 0.05 eV. Detailed description of the XPES study of the mineral surface is given in [5, 6].

The efficiency of mineral treatment with anolyte and HCl solution was estimated by the intensity of change in the physicochemical and electrical (ζ potential) properties of the liquid phase in the mineral suspension and mineral particles, respectively. The ζ potential was measured by the method of dynamic (electrophoretic) light scattering using a Zetasizer Nano ZS universal system for study of nanoparticles (Malvern Instruments).

The panoramic spectra of surfaces of the studied minerals contain the characteristic peaks of the frame levels of Ta, Nb, Zr, Fe, Mn, O, and Si. The photoelectron spectrum of the Ta 4*f* level in the composition of columbite and tantalite is characterized by the spin–orbital duplet of Ta 4*f*_{3/2} and Ta 4*f*_{1/2} with the positions of maxima ($E_{\text{bond}} \sim 26.0$ and 27.9 eV) corresponding to those of Ta₂O₅ [7]. The duplet Nb 3*d* ($E_{\text{bond}} = 207.0$ eV and ~208.9 eV) corresponds to the chemical state of Nb₂O₅ [8].

The spectrum of Mn 2*p* contains the following maxima: $E_{\text{bond}} \sim 640.2$, 641.1, 641.9, 642.6, and 643.6 eV. The first two of them are related to the MnO state, i.e., Mn(II); others, to Mn(IV) [9]. The spectrum of Fe 2*p*_{3/2} is approximated using the parameters from [10], and three components were distinguished: the peak at 709.5 eV corresponds to Fe²⁺ bonded with oxygen; the peaks at 711.2 and 713.3 eV are explained by Fe³⁺ in the oxide and hydroxide states, respectively.

Two components with bond energies $E_{\text{bond}} \sim 183.0$ and 185.1 eV typical of those of zirconium atoms in the ZrSiO₄ structure were identified in the XPES of Zr 3*d*. Two chemical states of silicon were distinguished in the Si 2*p* spectrum [11, 12]: Si in the composition of zircon ($E_{\text{bond}} = 101.7$ –102.1 eV) and Si atoms bonded into the chemical states of SiO₂ and Si–OH ($E_{\text{bond}} = 103.0$ –103.2 eV). The peak of the O 1*s* level of oxygen atoms in the studied zircon samples may occur as a

superposition of two components corresponding to threefold oxygen in the ZrSiO₄ structure with $E_{\text{bond}} = 531.1$ –531.3 eV and to oxygen atoms in the composition of defect groups like SiO₃²⁻ and SiO₂⁰ with $E_{\text{bond}} = 532.0$ –532.3 eV [11] (Table 1).

Analysis of the XPES data showed that treatment of rare-metal minerals with HCl solution and anolyte did not have a significant influence on the chemical state of Ta, Nb, and Zr atoms in the composition of the minerals (Table 1). The major effect from the physicochemical influence of acid solutions on the valent state of atoms on the mineral surface was reflected in the processes of oxidation of iron atoms with the transition of Fe(II) into Fe(III) for columbite and tantalite (Figs. 1a, 1b) and in destruction of the zircon surface with the formation of oxygen–vacancy defects (Figs. 1c, 1d).

Treatment of tantalite with anolyte resulted in a total increase in the concentration of Fe(III) by 29.5 at % with significant predomination of the hydroxide phase Fe(III)–OH (Table 1). Upon the contact of the mineral with the HCl solution, the total increase in Fe(III)–O and Fe(III)–OH contents was 10.7 at %.

Application of the HCl solution for columbite did not result in a significant increase in the surface concentration of Fe(III), whereas treatment of the mineral with anolyte resulted in intense oxidation of iron atoms with the transition of Fe(II) into Fe(III) (Table 1). In this case, almost all surface iron (96.5 at %) occurred in the trivalent state; the portion of hydroxyl (Fe(III)–OH) was 64.2 at %. In addition to the change in the chemical state of Fe surface atoms in the composition of columbite, treatment of the mineral with anolyte, as well as with the HCl solution, resulted in an increase in the surface concentration of Mn(II), proportionally to the decrease in the concentration of Mn(IV) (Table 1), presumably due to the reduction of Mn(IV) to Mn(II) atoms.

XPES of Si 2*p* and O 1*s* in zircon provide evidence for a significant change in the structural and chemical states of atoms on the mineral surface as a result of treatment with acid solutions. Analysis of the peak from the Si 2*p* level of Si atoms (Figs. 1c, 1d) showed that leaching with solutions resulted in transition of some Si atoms (from 4 to 9 at %) from the state of ZrSiO₄ to a chemical state close to that of SiO₂⁰ (Table 1). The spectra of the frame states of O 1*s* was characterized by a significant increase in the component with $E_{\text{bond}} = 532.3$ eV corresponding to oxygen atoms in the defect surface groups with the structure of SiO₃²⁻ and SiO₂⁰ [11] upon treatment of the mineral with the HCl solution (Table 1).

Based on study of the changes in the physicochemical properties and composition of the liquid phase of mineral suspensions using anolyte, we observed an

Table 1. Change in the phase composition of the surface of tantalite, columbite, and zircon as a result of treatment of mineral samples with the HCl solution and anolyte, at %

Mineral	XPES peak	E_{bond} , eV	Correspondence of the peak	at %		
				initial	HCl	anolyte
Tantalite	Ta 4 <i>f</i>	26.0	Ta ₂ O ₅	54.9	55.9	56.8
		27.9		45.1	44.1	43.2
	Nb 3 <i>d</i>	206.9	Nb ₂ O ₅	58.7	58.1	60.6
		208.9		41.3	41.9	39.4
	Fe 2 <i>p</i>	709.5	Fe(II)–O	34.4	23.8	5.0
		711.2	Fe(III)–O	52.3	58.3	36.7
713.2		Fe(III)–OH	13.2	18.0	58.4	
Columbite	Nb 3 <i>d</i>	207.1	Nb ₂ O ₅	60.5	60.8	60.2
		209.9		39.5	39.2	39.8
	Fe 2 <i>p</i>	709.5	Fe(II)–O	19.7	17.6	3.5
		711.2	Fe(III)–O	52.1	56.3	32.4
		713.2	Fe(III)–OH	28.2	25.8	64.2
	Mn 2 <i>p</i>	640.2	Mn(II) MnO	57.0	65.8	60.5
		641.1				
		641.9	Mn(IV) MnO ₂	43.0	34.2	39.5
642.7						
Zircon	Zr 3 <i>d</i>	183.0–183.1	ZrSiO ₄	56.7	58.9	56.6
		185.0–185.1		43.3	41.1	43.3
	Si 2 <i>p</i>	101.7–102.1	ZrSiO ₄	39.3	35.1	30.2
		103.0–103.2	SiO ₂ , Si–OH	60.8	64.8	69.8
	O 1 <i>s</i>	531.1–531.3	ZrSiO ₄	49.9	32.6	45.6
		532.0–532.3	SiO ₃ ²⁻ , SiO ₂ ⁰	50.1	67.4	54.4

increase in the concentration of Fe, Mn, and Si ions in solution by a factor of 1.2–1.5 in relation to treatment of minerals with the HCl solution. After treatment of columbite with the anolyte solution, the concentration of Fe(III) in the liquid phase of the mineral suspension (6.3×10^{-8} mg/cm²) increased by a factor of 8.6, which corresponded to the concentration (0.73×10^{-8} mg/cm²) in the HCl solution. Most likely, this fact is explained by active absorption of oxygen by the columbite surface, which is evident from the change in the redox potential of the anolyte solution from +845 to +300 mV.

Thus, treatment of mineral suspensions with anolyte stimulated more effective dissolution of iron- and silicate-bearing films from the mineral surface in comparison with the HCl solution applied in standard technologies, as well as active oxidation of divalent iron into the trivalent state in the crystal lattice of columbite and tantalite. The data of spectroscopic and physicochemical studies are supported by the results of measurements of the electrokinetic potential of minerals in an aqueous and acidic environment (Table 2).

The crystal structure of the columbite-group minerals corresponds to the structural type of brookite with a distorted package of oxygen atoms along the *a* axis [13]. The cations (Nb, Ta) and (Fe, Mn) occupy one-half of the octahedral sites forming corrugated columns along the *c* axis. Layered ordering of two (Nb, Ta) and one (Fe, Mn) columns occurs along the *a* axis [13].

The surface layer of minerals is characterized by the presence of positively charged cations Fe(II) and Mn(II), as well as hydrated iron oxides as surface

Table 2. Change in the electrokinetic potential of tantalite, columbite, and zircon as a result of treatment of minerals with anolyte and the HCl solution

Treatment	pH	Eh, mV	ζ-Potential, mV		
			columbite	tantalite	zircon
H ₂ O _{dist}	7	280	–24.8	–22.4	–16.6
Anolyte	3.5	950	2.4	3.1	–8.6
HCl solution	3.5	490	9.4	1.6	10.2

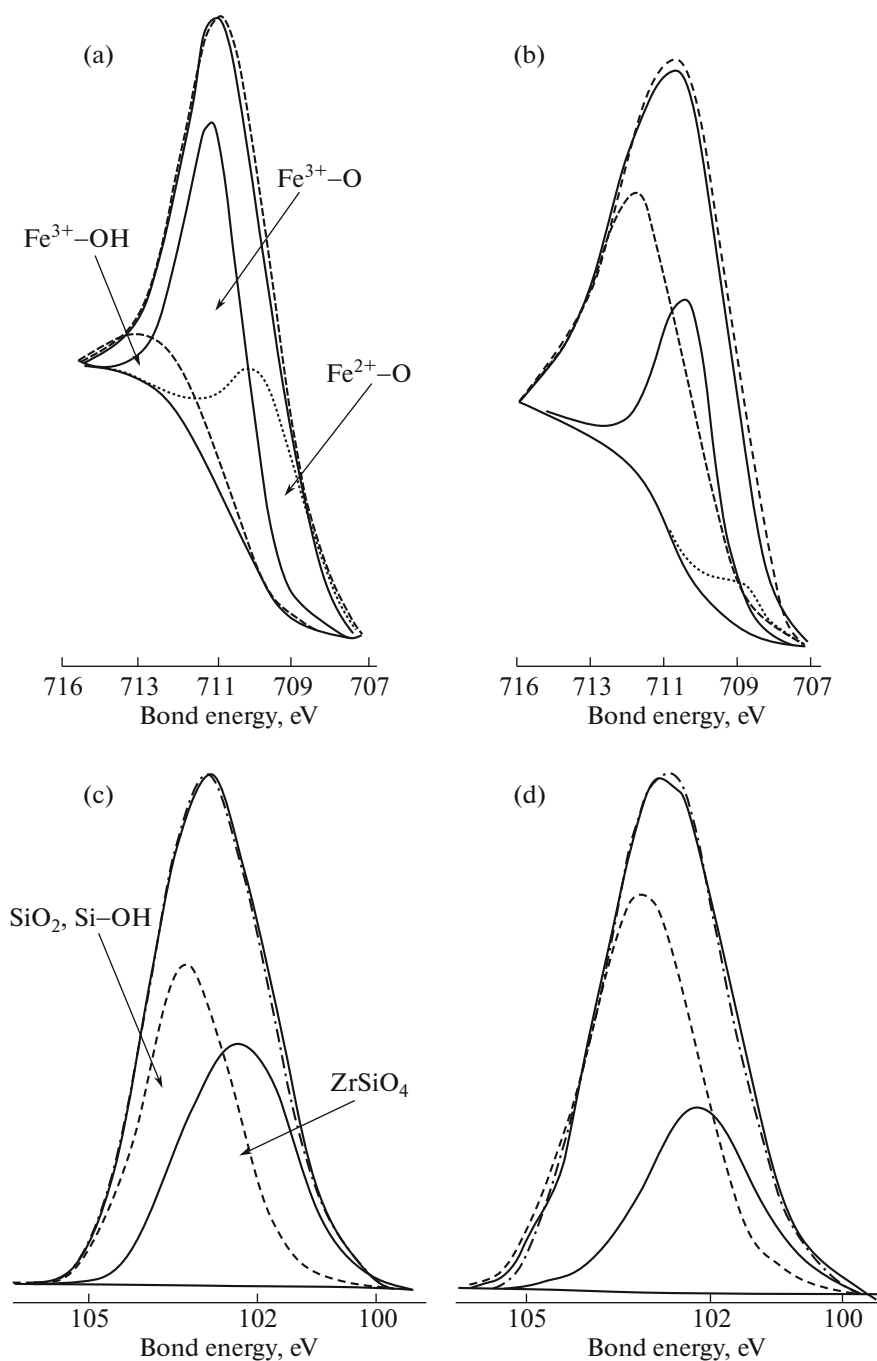


Fig. 1. XPS of the Fe $2p$ level for the surface of tantalite particles (a, b) and Si $2p$ level in the composition of zircon (c, d) before (a, c) and after (b, d) treatment with anolyte.

phases. The electric potential of the surface of mineral particles suspended in the liquid phase is controlled by the process of ion dissolution from the surface of crystals and by their transition into the liquid phase and the appearance of a charge on the crystal surface upon dissolution [14]. Therefore, Fe and Mn will be the potential-forming ions near the surface of columbite and tantalite, whereas the hydroxyl groups of the liquid phase (hydroxide anions) will be the counterions,

which determines the negative sign of the ζ potential of columbite and tantalite in a neutral environment with pH 7 (Table 2).

Addition of the HCl solution into the system resulted in selective adsorption of chloride ions on the columbite (tantalite) surface. An excessive negative charge was formed on the mineral surface, and an excessive positive charge (hydrogen ions) was formed in the contacting layer of the solution; i.e. a double

electric layer (DEL) was formed at the interphase surface. The diffusive part of DEL is positive, and, therefore, the ζ potential has positive values (Table 2).

Upon treatment of minerals with anolyte, the surface of particles absorbed oxygen intensely, which stimulated oxidation of Fe(II) to Fe(III), according to the scheme $\text{Fe(II)} + \text{O}_2 \rightarrow \text{Fe(III)} + \text{e}^-$. This was accompanied by dissolution of hydroxide surface films and leaching of Fe(III) and Mn(II) cations from the crystal lattice of the surface layer of columbite, which resulted in violation of the electroneutrality of the surface and formation of excessive negative charge (anions of the liquid phase) on the mineral surface and excessive positive charge (hydrogen ions) in the contacting layer of the solution. Thus, the DEL was formed at the interphase surface. The diffusive part of DEL and, therefore, the electrokinetic potential are positive (Table 2).

The change in the ζ potential of zircon upon treatment with acid solutions (Table 2) was in agreement with the data of [14, 15]: with increasing pH of the liquid phase, the value of the electrokinetic potential of the minerals migrated towards negative values.

CONCLUSION

Based on the complex of investigations performed, we revealed the mechanism of structural and chemical transformations of the surface of tantalite, columbite, and zircons during leaching of minerals with acid solutions. This mechanism included activation of the process of dissolution of iron- and silicate-bearing films from the surface of minerals and intense oxidation of Fe atoms in the surface layer of tantalite and columbite with the transition of Fe(II) to Fe(III) and destruction of the zircon surface with the formation of the oxygen–vacancy defects like SiO_3^{2-} and SiO_2^0 upon interaction with anolyte.

ACKNOWLEDGMENTS

This study was supported by the Russian Science Foundation, project no. 16-17-10061.

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Translated by A. Bobrov