Optical properties of PEO coatings on niobium formed in borate and tungstate electrolytes

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Introduction

Anodizing valve metals above the breakdown voltage leads to intense generation of spark discharges accompanied by gas evolution. This process, known as Plasma Electrolytic Oxidation (PEO), is commonly used to obtain multilayer gradient coatings with high adhesion to the metal substrate and developed morphology. PEO coatings on niobium have been obtained in aqueous electrolytes based on silicates, phosphates, and aluminates*, which are traditionally used for PEO processing of other valve metals. It is of interest to expand the range of electrolytes used for PEO processing of niobium. It is known that the PEO treatment of Ti in 0.1M $Na_2B_4O_7$ leads to the formation of coatings based on TiO_2 that are photoactive in UV light, while W-enriched PEO coatings formed in 0.1 M Na_2WO_4 can have photoactivity as in UV and Vis irradiation. It is of interest to use these electrolytes for the PEO processing of niobium. For a preliminary assessment of the photoactivity of PEO coatings, it is necessary to evaluate their optical properties.

* Babaei K., Fattahalhosseini A., Chaharmahali R. A review on plasma electrolytic oxidation (PEO) of niobium: Mechanism, properties and applications, Surfaces and Interfaces. 2020. V. 21. Paper 100719.

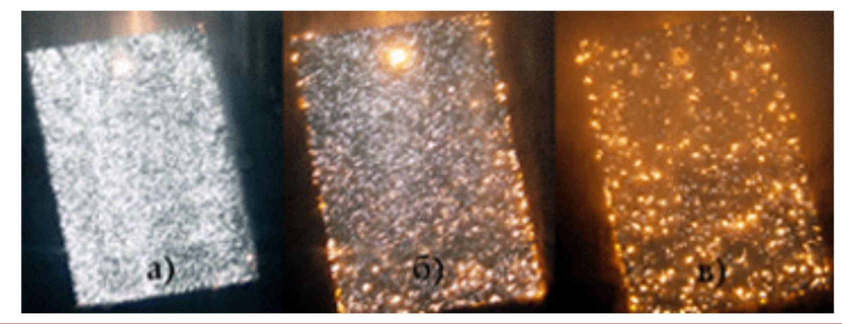

Figure 1. Evolution of discharges as the oxide layer grows

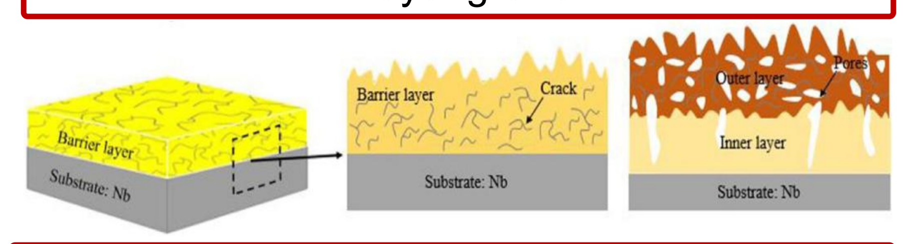

Figure 2. Schematic model of the formation of PEO coatings on Nb

Purpose of the work

Plasma electrolytic formation of Nb_2O_5 and Nb_2O_5+WO_3 coatings on niobium in borate and tungstate electrolytes and studying their optical properties.

Objects and Methods

- The samples (2x2 cm) for PEO processing were made from Nb foil annealed at 1700°C for 1 h.
- The objects under study were PEO-coated niobium samples obtained in three different electrolytes by varying the current density and process time (Table).
- The surface morphology was studied on a Hitachi S5500 high-resolution scanning electron microscope (Japan) equipped with a ThermoScientific (USA) attachment for energy-dispersive X-ray analysis.
- Diffuse reflection spectra of the resulting PEO coatings were recorded using an SF-56 spectrophotometer (Russia).

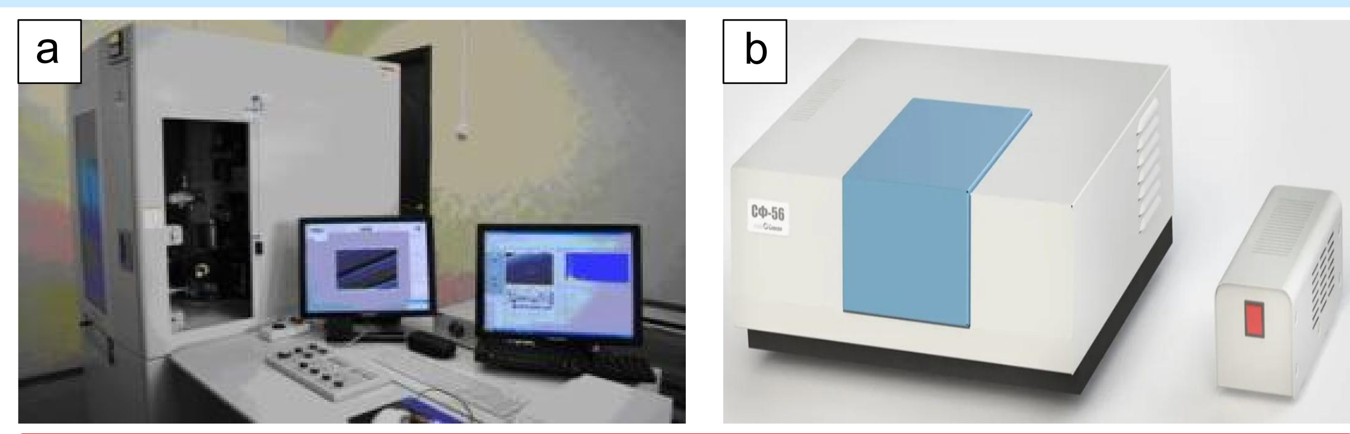

Figure 3. (a) Hitachi S5500 high-resolution scanning electron microscope, (b) SF-56 spectrophotometer

Results

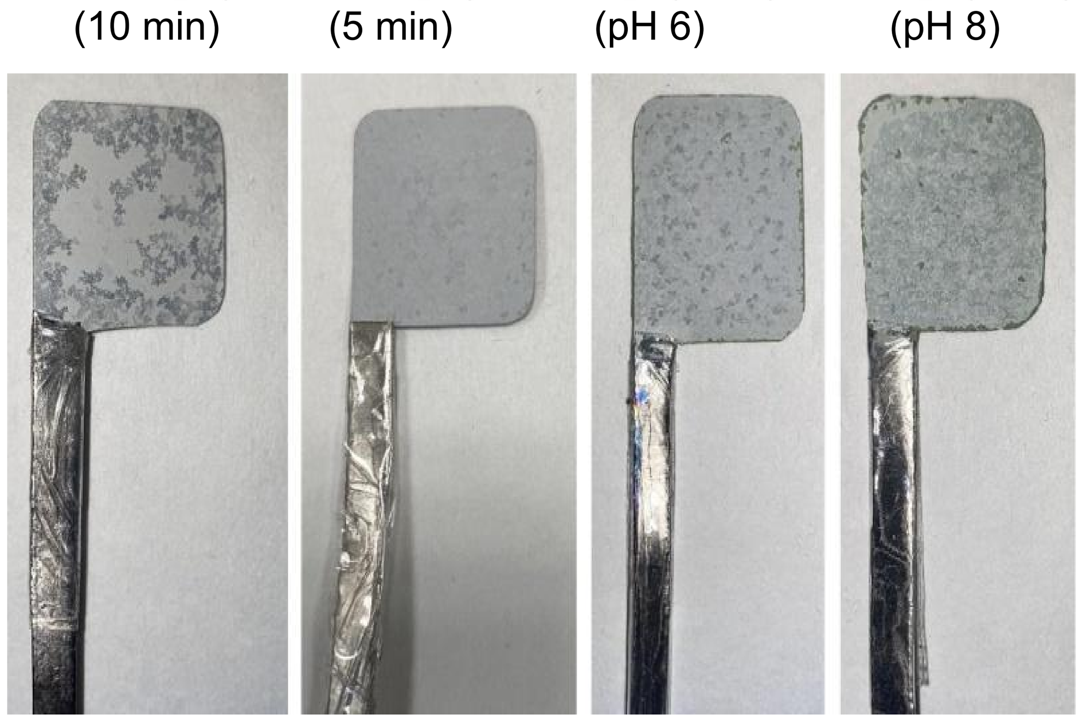

Figure 4. Photos of the obtained samples

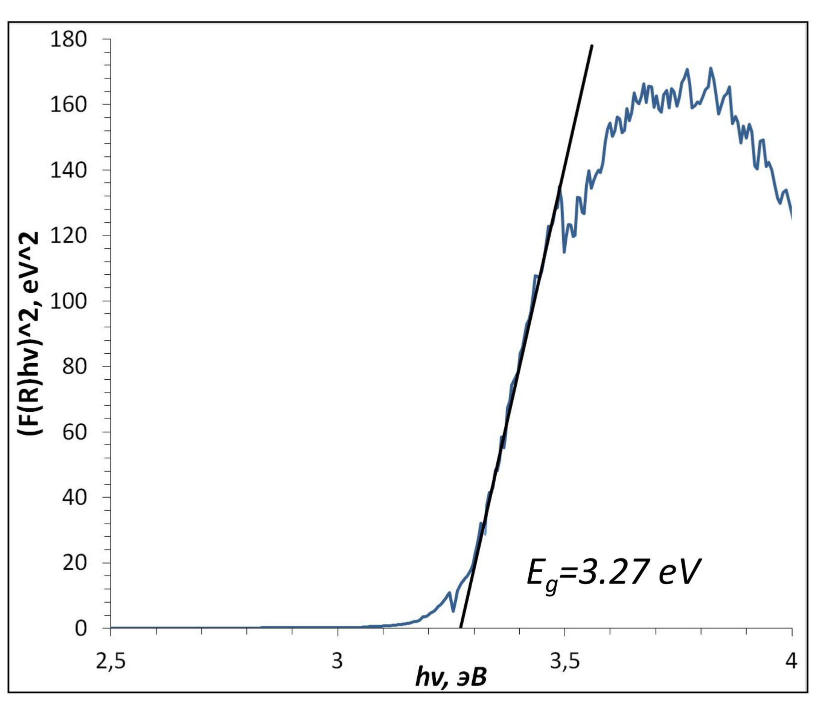

Figure 5. Tauc plot for Nb/Nb_2O_5 (10 min)

The band gap was estimated from Tauc plots using the Kubelka–Munk function.

Table. Influence of the electrolyte and the PEO processing mode on the energy of the direct allowed electronic transition E_g of the formed composites

Composite	Electrolyte	j, A/cm²	t, min	E_g, eV
Nb/Nb_2O_5 (10 min)	0.1M $Na_2B_4O_7$	0.1	10	3.27±0.01
Nb/Nb_2O_5 (5 min)	0.1M $Na_2B_4O_7$	0.1	5	3.27±0.01
$Nb/Nb_2O_5/WO_3$ (pH 6)	0.1M Na_2WO_4+ 0.1M CH_3COOH	0.1	5	3.25±0.01
$Nb/Nb_2O_5/WO_3$ (pH 8)	0.1M Na_2WO_4	0.2	5	3.13±0.01

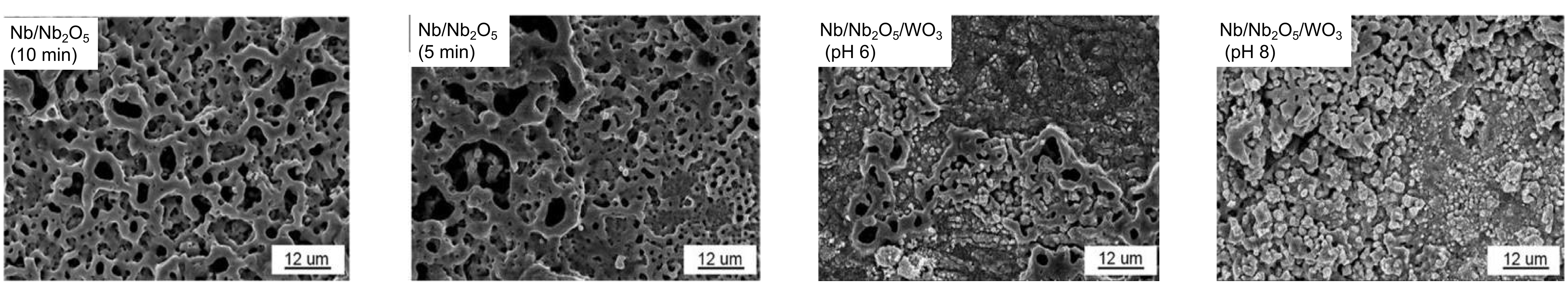

Figure 6. SEM images of PEO-coated niobium samples

According to the results obtained by the diffuse reflection method, the band gap energy for a direct allowed transition is 3.13–3.25 eV for Nb/Nb_2O_5 composites, and Eg = 3.27 eV for $Nb/Nb_2O_5/WO_3$. This is lower than the band gap of the Nb_2O_5 films obtained sol-gel method (E_g = 3.43 eV). The decrease in the band gap for Nb/Nb_2O_5 can be associated with the appearance of defects as a result of deformation of Nb_2O_5 under molten B_2O_3, which is formed due to the thermolysis of $Na_2B_4O_7$ around the electrical breakdown channels. The decrease in the band gap for W-enriched composites may be due to the formation of Nb_2O_5/WO_3 heterostructures, in which Eg(WO_3) ≈ 2.8 eV.

Conclusions

In this work, the optical properties of samples of PEO coatings formed on niobium in borate and tungstate electrolytes are studied for the first time. It is shown that PEO layers on niobium have a band gap smaller than Nb_2O_5 films obtained by other methods.

The work was carried out within the framework of state assignments of the Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences No. FWFN (0205)-2022-0001 and with the support of the program of applied research and development of students and postgraduates of the Federal State Budgetary Educational Institution of Higher Education "Petrozavodsk State University", providing a significant contribution to the innovative development of economic and social sectors Republic of Karelia, for the period 2022-2023."