

## Synthesis of vanadium sesquioxide films for the protection of high-temperature superconductor ribbons

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We obtained thin films (coatings) of  $V_2O_3$  on conducting substrates for potential use as a protective layer on superconducting ribbons. The coatings were obtained by thermal oxidation of pure vanadium ribbons or by electrochemical deposition from a solution of sodium vanadate onto copper substrate. We have studied the dependence of the structure and phase composition of the obtained films as a function of the conditions of their synthesis. For films obtained by thermal oxidation, we obtained the temperature dependences of their resistance in the 77–300 K temperature range.

**Keywords:** high temperature superconductor, Mott insulator, metal–insulator transition, vanadium sesquioxide.

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The windings of magnetic systems (especially superconducting ones) are traditionally fabricated with reliable insulation that prevents turn-to-turn short-circuiting. Thin-layer (1–4  $\mu\text{m}$ ) high-temperature superconductor (HTSC) materials with a superconducting transition temperature of 90–92 K have been developed in recent decades. Existing HTSC-based electromagnet winding wires have a significant drawback: low velocity of propagation of the normal zone along a conductor [1]. It is 1–2 orders of magnitude lower than the corresponding velocity in low-temperature superconductors and does not exceed 10 cm/s at near-critical currents [2]. This induces local ohmic heating and destruction of the material. It has been proposed several years ago to use non-insulated superconducting windings in the form of ribbon double pancakes (in most cases, these are ribbons with a Cu coating) [3]. In a non-insulated winding, the normal zone propagates not only along the superconductor, but also in the transverse (radial) direction, enhancing the thermomagnetic winding stability.

The downside of non-insulated windings is the time lag between the supplied current and the magnetic field. The characteristic delay time is  $\tau = L/R_r$ , where  $L$  is the inductance of a superconducting winding with insulation and  $R_r$  is the radial resistance of a non-insulated winding.

The lack of insulation makes it difficult for the winding to operate with a time-varying current of frequency  $\omega > 1/\tau$ . In view of this, the formation of an additional coating layer on HTSC ribbons, which has a high resistance at the operating temperature of the winding and undergoes a transition to a state with a higher electrical conductivity when heated, is an important and relevant scientific challenge that needs to be addressed in order to produce new and better protected HTSC structures for windings of magnetic systems. Vanadium sesquioxide  $V_2O_3$  is a candidate coating of this kind. This oxide exhibits the so-

called Mott metal–insulator phase transition at 140 K [4,5] wherein its resistivity changes by more than seven orders of magnitude [6]. Magnetron sputtering is the method for producing  $V_2O_3$  films that has advanced the most in recent years [7]; however, it is expensive and ill-suited for deposition onto long ribbons on an industrial scale.

In the present study, samples of  $V_2O_3$  thin films (coatings) were synthesized on conducting substrates for inclusion into a superconducting ribbon winding. Vanadium (0.1-mm-thick with a specific conductivity of  $\sim 40 \cdot 10^5 \text{ S/m}$ ) and copper (0.06-mm-thick with a specific conductivity of  $\sim 60 \cdot 10^6 \text{ S/m}$ ) used in traditional HTSC ribbons served as substrates for the films. The coating was formed in two ways: by thermal oxidation of undoped vanadium ribbons and electrochemical deposition of amorphous hydrated vanadium sesquioxide from a sodium vanadate solution onto vanadium or copper substrates.

Thermal oxidation was performed in an SVF-1200X80 vacuum furnace with its working volume evacuated to at least 0.01 Torr by a rotary forevacuum pump. Sheet vanadium samples were heated at a rate of  $\sim 20^\circ\text{C/min}$  from room temperature to 800–900°C and annealed in vacuum for 60 min. The residual pressure was measured by a barometric sensor and remained within the range from  $10^{-2}$  to  $10^{-1}$  Torr. The cooling rate was 7–15°C/min for different samples.

The structure and phase composition of the obtained films were examined by X-ray diffraction analysis methods with a Siemens Kristalloflex D5000 X-ray diffractometer in monochromatic  $\text{CuK}\alpha$ -radiation in the „reflection“ geometry (scattering angles  $2\theta = 20\text{--}110^\circ$ ). The morphology and elemental composition were studied using a Hitachi SU1510 scanning electron microscope with a built-in spectrometer designed for energy-dispersive analysis.

In the case of vacuum thermal oxidation synthesis, the highest-quality coating with strong adhesion to the substrate was obtained on metallic vanadium. The estimated thicknesses of all films fell within the range of 1–10  $\mu\text{m}$ . Samples of  $\text{V}_2\text{O}_3$  coatings on metallic vanadium oxidized thermally at a temperature of 900°C and an air pressure on the order of  $10^{-1}$  Torr are prone to embrittlement (due presumably to the diffusion of a fraction of oxygen into the bulk of vanadium).

After cooling to room temperature at a rate of  $\sim 7^\circ\text{C}/\text{min}$ , the samples assumed a black matte color. The electron microscope images (Fig. 1, *a*) reveal that the coating has the form of platelets oriented vertically relative to the surface. The average values of the transverse size of these platelets and their thickness are 1 and 0.01  $\mu\text{m}$ , respectively. Light sanding with a soft material removes them, leaving a continuous coating with rare cracked regions ( $\sim 1\%$  by area).

Images of the cross section of the sample (Fig. 1, *b*) revealed that the coating takes the form of a monolithic base on the metal surface with a transition to a layer of the above-mentioned vertically oriented platelets. Under the specified conditions, the thickness of this monolithic base is  $\sim 0.5 \mu\text{m}$ , and the thickness of the upper layer of nanoplatelets is  $\sim 1 \mu\text{m}$ . A similar structure of vanadium sesquioxide with vertically oriented nanoplatelets 330 nm in height was obtained in [8] by reactive magnetron sputtering.

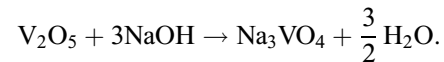
At the same time, a different type of coating was obtained at a higher cooling rate of samples ( $\sim 15^\circ\text{C}/\text{min}$ ). Light and dark regions are visible in the electron microscope images. Viewed under higher magnification, these light and dark coating areas are the regions of vertically oriented nanoplatelets and a dense film with relatively rare pores (the areal fraction of pores ranged from 5 to 10%).

The X-ray diffraction patterns of coatings are dominated by the lines of metallic vanadium and  $\text{V}_2\text{O}_3$ , but the relative intensities of the  $\text{V}_2\text{O}_3$  lines differ from the reference ones for powders. Specifically, the intensity ratio of lines corresponding to 33.16 and 24.37° is 1.3 for the reference and 0.7 for the obtained samples. X-ray diffraction analysis did not reveal the presence of other vanadium oxide phases in the synthesized films. Figure 2, *a* shows the diffraction pattern of the sample with a coating in the form of nanoplatelets.

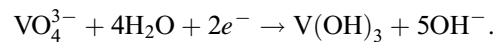
Temperature dependences  $R(T)$  of resistance of the  $\text{V}_2\text{O}_3$  film samples on vanadium were measured within the range from room temperature to 77 K by passing a current of 1–10 mA across the sample plane. To eliminate the effect of voltage drop in lead-in wires, a four-wire circuit was used. These dependences demonstrate a  $\sim 20$ -fold change in resistance upon cooling from 300 to 77 K; the greatest slope of the  $R(T)$  dependence is observed at  $T \sim 160$  K. The relative resistance variation for single-crystal  $\text{V}_2\text{O}_3$  films [9,10] is  $\sim 10^7$ , which is almost six orders of magnitude greater than the indicated ratio for the obtained coatings. At the same time, the relative change in resistance is  $\sim 10^3$  [11] for layers synthesized from  $\text{V}_2\text{O}_3$  powders in

polymer binders and just  $\sim 20$ –30 [12] for nanocrystalline films on glass substrates. Thus, the proposed method for production of  $\text{V}_2\text{O}_3$  films on vanadium requires further refinement to increase the magnitude of resistance variation during the phase transition.

It is known [13] that coatings consisting of lower vanadium oxides are easy to obtain by electrochemical deposition from aqueous solutions of vanadates. This method has an advantage in that coatings may be deposited on essentially any conductive surface. Thus, no buffer layer of metallic vanadium is required. Therefore, this method was also tested. The electrochemical synthesis of films was carried out as follows. The electrolyte was prepared from 1/400 mol of  $\text{V}_2\text{O}_5$  powder and 3/200 mol of sodium hydroxide (NaOH) in the form of a 1 M solution; distilled water was then added up to 50 ml so that the vanadium concentration was 0.1 g-atom/l. An aqueous solution of sodium orthovanadate  $\text{Na}_3\text{VO}_4$  was obtained as a result:

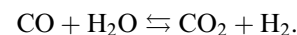
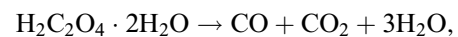


Copper plates  $4 \times 30$  mm in size served as the cathode. A graphite anode was used. The cathode and anode spaces were separated by a porous polypropylene filter with a pore size of approximately 20  $\mu\text{m}$ . The distance between the electrodes was 2–4 cm. The current in different experiments varied from 0.01 to 0.07 A; this required a voltage of approximately 5–7 V. This resulted in deposition of a  $\text{V}(\text{OH})_3$  layer onto the copper substrate:

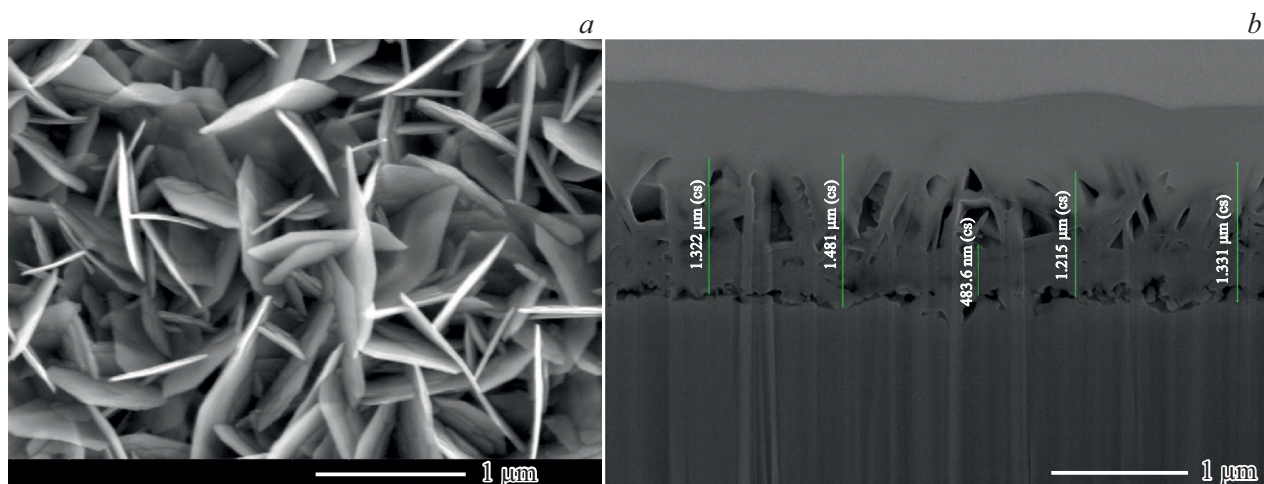


A  $\text{V}(\text{OH})_3$  film cannot be deposited onto a smooth copper surface due to poor mechanical adhesion. Therefore, the copper ribbons were etched prior to electrolysis for 1–2 min with 65% nitric acid diluted in a ratio of 1:2 or 1:3. Etched samples appeared matte. The deposition yield by current (determined from the sample weight) was as low as  $\sim 4\%$ ; i.e., the current flow contributed mostly to the formation of hydrogen.

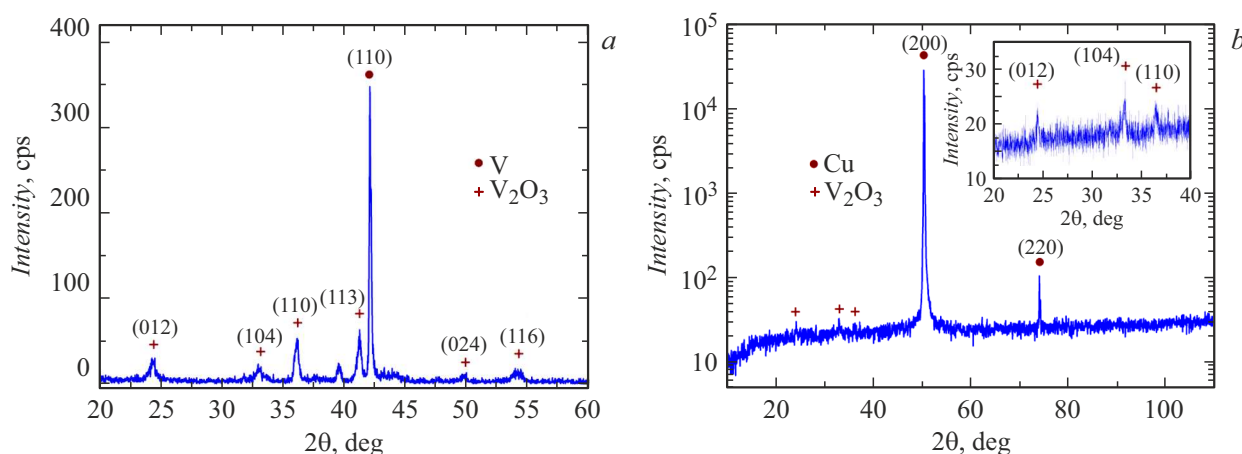
Following electrolysis, the films were annealed at 600°C in a reducing  $\text{Ar} + \text{CO}$  atmosphere. Oxalic acid was used to generate carbon monoxide in the annealing process:



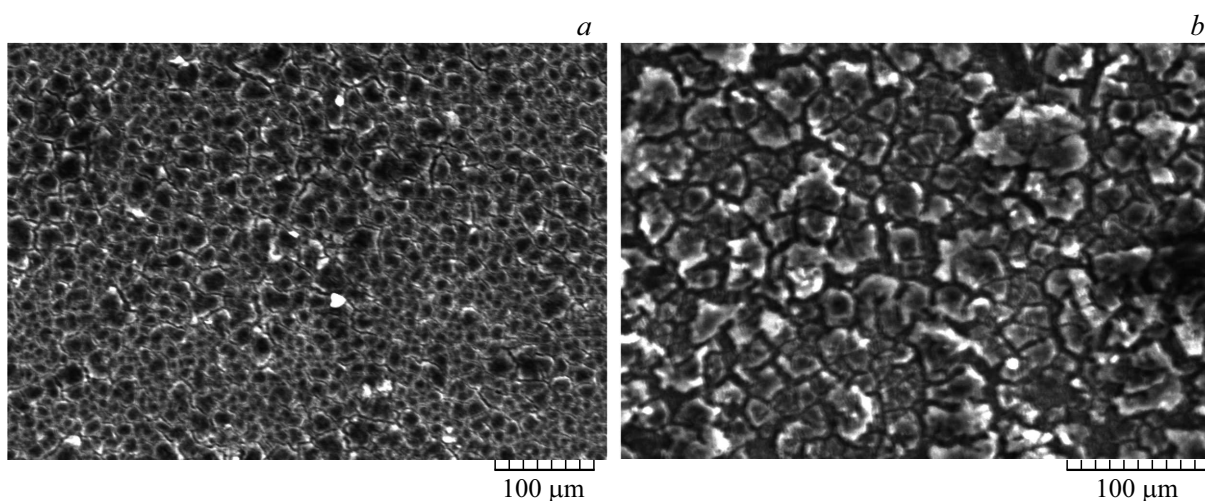
The electron microscope examination of films prepared by electrolysis revealed that they consist of individual tiles with cracks between them. Copper was visible in the cracks. The tile area and the width of cracks depend on the electrolysis parameters. Both the tile size and the width and depth of cracks increase with film thickness. Figure 3 presents the images of coatings of different thickness obtained using an electron microscope. A thin film (Fig. 3, *a*) was synthesized by electrolysis in 10 min at a current of 0.1 A; a thick film (Fig. 3, *b*) was prepared in 2 h at a current of 0.2 A. The



**Figure 1.** Electron microscope images of  $V_2O_3$  coatings on vanadium. *a* — Surface, *b* — cross section (measured coating thicknesses are indicated). The sample is thermally oxidized vanadium ( $T_{ox} = 900^\circ\text{C}$ , and the oxidation time is 60 min).



**Figure 2.** X-ray diffraction patterns of different samples. *a* — Thermally oxidized  $V_2O_3$  on vanadium with a nanoplatelet coating structure; *b* — electrochemically deposited  $V_2O_3$  on a copper ribbon (film with a thickness of  $\sim 0.3 \mu\text{m}$ ).



**Figure 3.**  $V_2O_3$  films of different thickness obtained by electrolysis on copper ribbons and imaged with an electron microscope. *a* — Film with a thickness of  $\sim 0.3 \mu\text{m}$ ; *b* — film with a thickness of  $\sim 3 \mu\text{m}$ .

estimated coating thicknesses are 0.3 and 3  $\mu\text{m}$ , respectively. The approximate size of fragments for these films is 3 and 30  $\mu\text{m}$ , respectively, and the ratio of thickness to fragment size is close to 1:10 in both cases. The width of cracks is comparable to the film thickness.

The diffraction patterns of the obtained annealed samples make it clear that vanadium is present in them in the form of  $\text{V}_2\text{O}_3$  (Fig. 2, *b*). The lines of vanadium sesquioxide are significantly weaker than the lines of copper. Owing to insufficient adhesion of the obtained coating to the copper substrate,  $R(T)$  measurements were not carried out; it is evident that this method is less well suited to achieving the stated research goal.

It can be concluded that of all the examined synthesis techniques, the method of oxidation of metallic vanadium in air currently appears to be the best suited for our research.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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