Vanadium sesquioxide nanostructure films for high-temperature superconductor tapes

© O.Y. Berezina, V.S. Ignahin, I.V. Sekirin, D.R. Kozorez, V.V. Putrolaynen, D.A. Yakovlev

Petrozavodsk State University, Petrozavodsk, Russia
E-mail: berezina@petrsu.ru

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The article describes a possible method for preventing the burnout of high-temperature superconductor tapes when alternating current flows. It is shown that a metal–insulator phase transition is observed in a film consisting of vanadium sesquioxide V_2O_3 nanowires and a polymer binder applied to copper foil. The results of a study of the phase composition, surface morphology, and temperature dependence of the film resistance in the range of 77–300 K are presented.

Keywords: high-temperature superconductor, electrospinning, metal–insulator transition, vanadium sesquioxide

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High-temperature superconductor (HTSC) tapes with a superconducting transition temperature of 90–92 K are used to construct superconducting magnetic systems of tokamaks, magnetic resonance imagers, and NMR spectrometric setups.

However, a section of a superconducting magnetic system in operation may transition from the superconducting state to the normal one under the influence of random thermal perturbations, which are commonly believed to be unpredictable and irreversible [1]. This transition to the normal state may lead to heating of an HTSC tape (due to the release of heat in the normal section of the superconductor) and failure of the magnetic system.

Interturn and interlayer insulation is crucial for stable operation of the system, but a lack of such insulation, which leads to automatic bypass of hot spots by current, would help suppress hazardous accidental local heating after the formation of the normal phase in the magnet [2].

The use of a non-insulated winding in the form of a Cu-coated tape [3] allows one to prevent HTSC coil failures due to the spread of normal zones both along and across the superconducting layers. However, the AC operation of this non-insulated winding is hampered by the delay between the current entering the winding and the magnetic field. The corresponding 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. A non-insulated winding cannot operate with a time-varying current with frequency $\omega > 1/\tau$; therefore, interturn and interlayer insulation is necessary.

Thus, it makes sense to introduce a layer, which acts as an insulator at a low operating temperature and when current is injected, but becomes conductive when the current drops and local heating occurs after the formation of a normal phase in the magnet winding, between the turns of HTSC tapes.

In order to shunt current effectively when a normal zone emerges, we propose to place copper foil coated with a film of a material with a metal–insulator phase transition (MIPT) between the HTSC tape layers: at temperatures $T < 90$ K, the film is dielectric and acts as an insulator between the HTSC tape turns, allowing for AC operation of HTSC coils; at $T > 140$ K, the film is metallic and shunts the current flowing through the HTSC tape in the normal state. Thus, heat will not be released within the HTSC layer, and it will remain undamaged.

Vanadium sesquioxide V_2O_3 has a suitable phase transition temperature (T_c). According to different sources, T_c is 140–155 K [4,5]. At room temperature, vanadium sesquioxide is a metal with rhombohedral lattice symmetry. When the temperature decreases to 140 K, the lattice symmetry is reduced to monoclinic and a transition to the semiconductor phase with band gap $E_g = 0.2$ eV occurs. A reverse transition is observed when the temperature increases [4].

A sharp change in both the structure and resistance, which may vary by as much as seven orders of magnitude, is induced by such transitions in bulk V_2O_3. Transitions in thin films are affected by the choice of a substrate, fabrication method, deposition conditions, and thickness. The magnitude and temperature of the transition also depend on the stoichiometry of V_2O_3, since the transition is sensitive to the vanadium and oxygen deficiency in the film [5,6]. For example, the resistance of V_2O_3 films synthesized on sapphire by pulsed laser deposition jumps by 4–7 orders of magnitude (depending on the deposition conditions) as a result of MIPT [7].

The aim of the present study is to fabricate thin films based on micro- and nanoparticles of V_2O_3 on copper tape with fine adhesion that exhibit a jump in resistance (2–3 orders of magnitude) during MIPT.

The process of film fabrication consisted of several stages: synthesis of vanadium pentoxide V_2O_5 nanowires

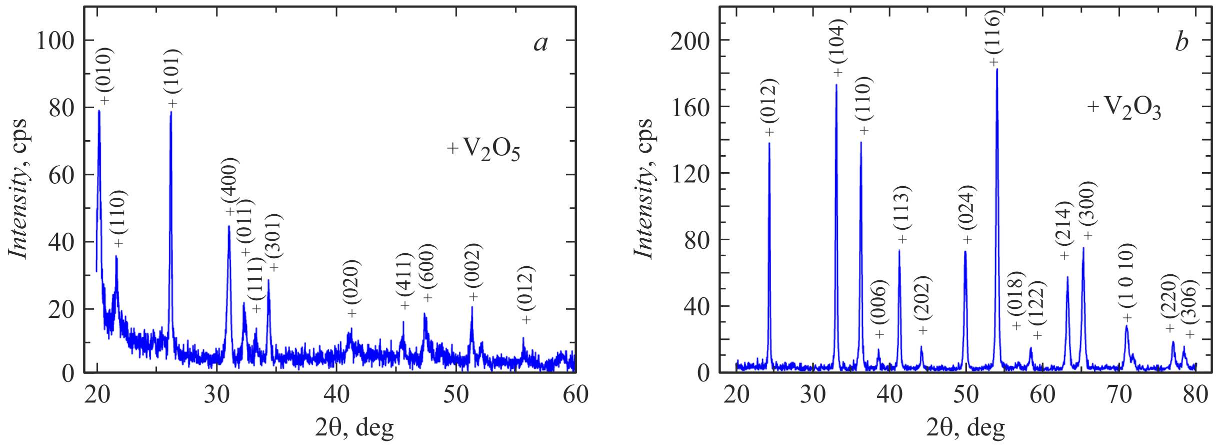

Figure 1. X-ray diffraction patterns of V_2O_5 nanowires after the first stage of annealing in air (*a*) and V_2O_3 nanowires after the second stage of annealing in argon (*b*).

by electrospinning; two-stage annealing of V_2O_5 wires for the production of V_2O_3 wires; preparation of a dispersion solution of V_2O_3 nanowires in ethyl alcohol with added polymer binder; deposition of this solution onto a copper substrate; drying.

The precursor for synthesis of V_2O_5 wires was prepared by dissolving V_2O_5 powder (analytical grade) in hydrogen peroxide (30 %) at a temperature of 7–10 °C in stoichiometric amounts. This results in the formation of red-brown monoperoxyvanadic acid:

$$V_2O_5 + 2H_2O_2 = 2HVO_2(O_2) + H_2O. \qquad (1)$$

The obtained solution of peroxide compounds was heated slowly to 60–80 °C. When heated, peroxyvanadic acid decomposes to form a neutral hexacoordinated vanadium complex

$$HVO_2(O_2) + 3H_2O = \left[VO(OH)_3(OH_2)_2\right]^0 + \frac{1}{2}O_2. \qquad (2)$$

Following condensation of this neutral precursor, the system transforms into a red-brown $V_2O_5 \cdot nH_2O$ gel via reaction

$$2\left[VO(OH)_3(OH_2)_2\right]^0 \rightarrow V_2O_5 \cdot 7H_2O. \qquad (3)$$

This $V_2O_5 \cdot 7H_2O$ was filtered, and 0.13 g/ml of high-molecular polyvinylpyrrolidone $(C_6H_9NO)_n$ (PVP) were added to it. PVP is needed as a polymer that reduces conductivity, which is a necessary prerequisite for electrospinning (the process of drawing of wires under the influence of a high-voltage electrostatic field).

Wires were obtained by electrospinning using a setup consisting of an NE-300 syringe pump, an INVR-30 high-voltage source, and a metal collector (aluminum foil). A syringe with the precursor was mounted in the syringe pump. A high voltage of 15–16 kV was applied between the syringe needle and the collector, which were spaced 16–18 cm apart. The precursor feed rate from the syringe was 0.25 ml/h. The result was a matrix of wires with a diameter of 450–550 nm.

Annealing in an OTF-1200X tubular programmable furnace was performed for 1 h at a temperature of 400 °C in air in order to remove PVP. The wire diameter after annealing was 350–400 nm.

The diffraction pattern obtained using a Siemens Kristalloflex D5000 X-ray diffractometer in monochromatic CuK_α radiation in the reflection geometry (scattering angles $2\theta = 20{-}110°$) is shown in Fig. 1, *a*. The results of X-ray diffraction analysis revealed that the wires consisted of vanadium pentoxide only.

Additional annealing in argon (1 atm) with added oxalic acid was performed for the purpose of reduction of V_2O_5 wires to V_2O_3 and crystallization. Carbon monoxide, which forms when oxalic acid decomposes, is a reducing agent:

$$H_2C_2O_4 \rightarrow H_2O + CO + CO_2. \qquad (4)$$

This annealing was performed at a temperature of 590 °C for 2 h and at 800 °C for 1.5 h; the approximate rate of heating to 590 °C (800 °C) was 15 °C/min (20 °C/min).

The X-ray diffraction pattern and the microphotographic image of V_2O_3 nanowires are shown in Figs. 1, *b* and 2, *a*, respectively. The results of X-ray diffraction analysis of nanowires revealed the presence of just one phase: V_2O_3.

The surface morphology and thickness of the film was analyzed using a Hitachi SU1510 scanning electron microscope (SEM). The wire diameter after annealing was 170–250 nm.

V_2O_3 films were applied to a copper tape, which is used in fabrication of HTSC tapes (thickness, 0.06 mm; specific conductivity, close to $60 \cdot 10^6$ S/m), in the following way. Low molecular weight K30 PVP powder was dissolved in ethyl alcohol (1 mg PVP per 1 ml of alcohol) and stirred with a magnetic stirrer for 5–10 min; after that, V_2O_3 nanowires (20 mg of wires per 1 ml of solution) were introduced into the solution and stirred for 3 min in an ultrasonic bath. The result was a suspension of wires in

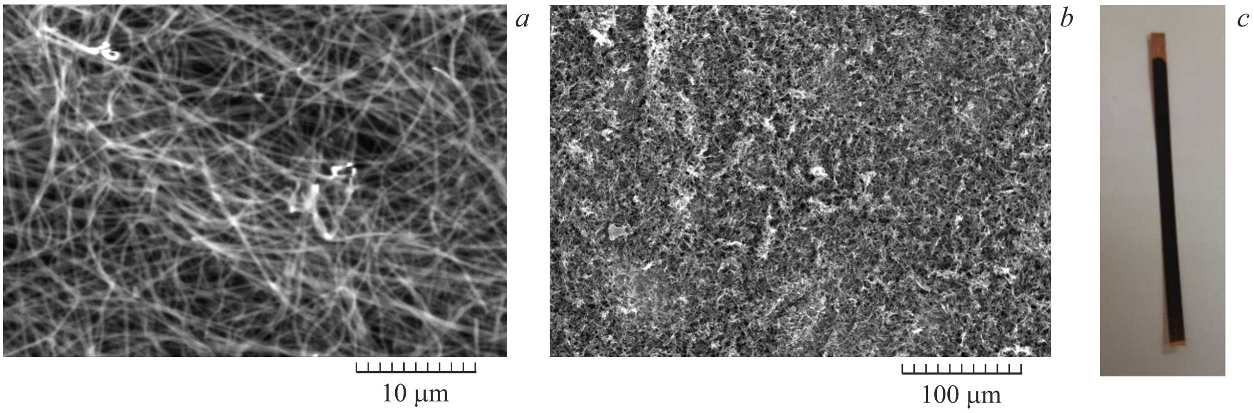

Figure 2. *a* — V_2O_3 nanowires imaged with a Hitachi SU1510 SEM (×3000); *b* — film of V_2O_3 nanowires on a copper tape imaged with a Hitachi SU1510 SEM (×300); *c* — photographic image of a copper tape with a V_2O_3 film.

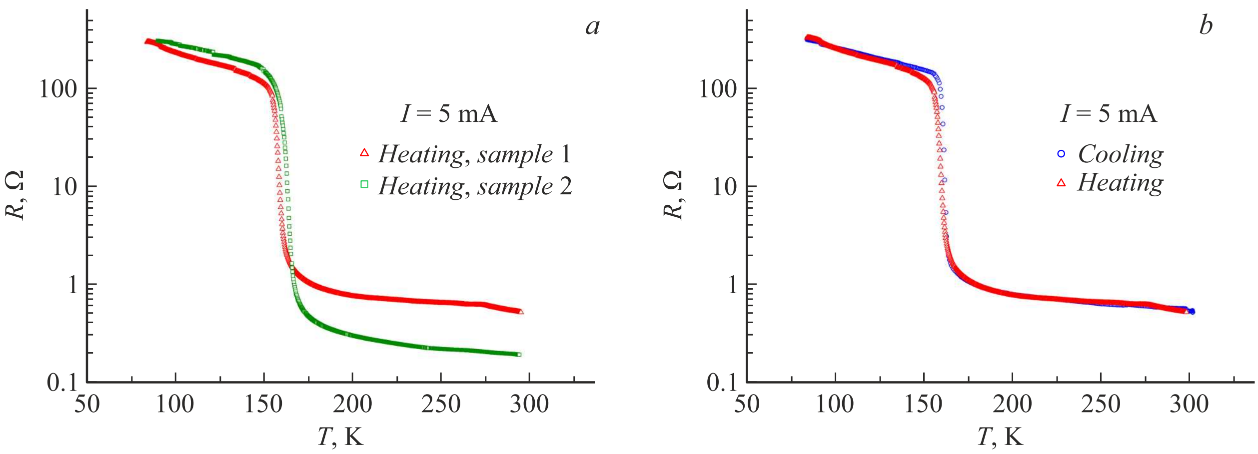

Figure 3. Temperature dependences of resistance of V_2O_3 films on the copper tape. *a* — Heating curves of two samples; *b* — cooling and heating curves of sample 1.

an alcohol solution of PVP. Polyvinylpyrrolidone served as a binder for the wires and promoted film adhesion to the copper tape. The prepared suspension was applied layer by layer to the copper tape. Layers were dried under an IR lamp to speed up the deposition. The deposition process was continued for as long as copper remained visible through the film. The microphotographic image of a film of V_2O_3 nanowires on a copper tape is presented in Fig. 2, *b*; the copper tape with a V_2O_3 film is shown in Fig. 2, *c*.

To measure the coating thickness, the coating on copper foil was cut with a blade. The measurement was carried out using a Hitachi SU1510 electron microscope with an EDX spectrometer. The average film thickness was 10–12 μm; it may be changed if necessary.

The mechanical properties were probed by verifying the stability of the V_2O_3 film on the copper tape bent with a radius of 5.5 cm. The tape with the film was then held in nitrogen vapor for 10 min and bent again. The film did not crumble or peel off.

The temperature dependences of resistance of samples were studied in a sealed copper cell. To cool the samples from room temperature to ~ 77 K, the cell was immersed in liquid nitrogen. Heating was performed by lifting the cell from the vessel with liquid nitrogen and holding it in air at room temperature. A current of 1–10 mA from a Keithley 2400 precision current source was passed across the sample through pressed copper contacts with an approximate area of 8 mm^2 in order to measure the resistance; the voltage across the sample was measured with a Keithley 2002 precision multimeter. A four-wire circuit was used to eliminate the effect of voltage drop in lead-in wires. The sample temperature was measured using an integrated *K*-type thermocouple in contact with the sample.

The measurement results are shown in Fig. 3.

All samples undergo a phase transition at a temperature of 155–160 K with the resistance changing by 2–3 orders of magnitude in the process of heating from 90 to 200 K.

Differences in the room-temperature film resistances and phase transition parameters of samples may be attributed to the variation of film thickness. For example, it was demonstrated in [8] that the MIPT parameters for epitaxial V_2O_3 films depend to a significant extent on thickness.

The results remained reproducible in measurements repeated both on the same day and a week later. Measurements over a more extended period are planned to be performed in the future.

The obtained MIPT parameters are comparable with the results reported in [9], where the resistance of V_2O_3 layers on a commercial HTSC tape changed by approximately three orders of magnitude.

Thus, a method for producing V_2O_3 films on a copper tape with fine adhesion, which allows one to wind the tape on a coil, was developed. The film resistance dropped by 2–3 orders of magnitude at a temperature of $150-170$ K. The developed coating may be used to protect HTSC tapes from burnout.

Other polymer binders are planned to be examined in the future with the aim of increasing the magnitude of resistance variation of V_2O_3 films during MIPT.

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Conflict of interest

The authors declare that they have no conflict of interest.

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