Development of apparatus and technology for creation of a superconducting niobium coating on the cryogyroscope rotor

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Abstract. The processes of creating a superconducting niobium coating on a cryogoscope rotor were considered. The conditions for the electrodeposition of superconducting niobium coatings from molten salt on rotors of a cryogenic gyroscope were determined. Niobium coatings obtained from molten salt were electrochemically polished and subsequently protective coating of niobium pentoxide was electroformed. The processes occurring during the electrodeposition, electropolishing and electrooxidation of niobium were considered. The equipment and technology for creating a superconducting niobium coating on the rotor of a cryogenic gyroscope was developed.

1. Introduction

The manufacture of a spherical rotor of a cryogenic gyroscope includes the next stages:
– the electrodeposition of a superconducting niobium coating on the substrate from the melt using a soluble anode and a rotating cathode [1];
– electrochemical and mechanical polishing of a superconducting niobium coating;
– electroformation of a protective niobium oxide film on the coating that to prevent degradation the superconducting properties of niobium.

Carbopyroceram was used as a rotor substrate material. The use of this material because it has a low density and is a conductive material and corrosion-resistant in the melt of alkali metal halides containing niobium salt [2]. Before electrodeposition of the superconducting coating, an annular cut was made on the spherical substrate along its equator. An annular cut is necessary that to provide a stable rotation of the rotor around one axis [3].

2. Experimental

For the creation of superconducting niobium coating on the rotor of a cryogyroscope a rotating electrode was used. It consists of two parts: top part is fixed; bottom part is rotating by digital controlled stirrer. Construction of the electrode provides the electrical contact in a random point of the sample and due to such contact a uniform surface smoothing is occurred.

Electrochemical polishing was carried out in a mixture of sulfuric and hydrofluoric acids H_2SO_4:HF (9:1) using the VoltaLab-40 PGZ301 dynamic electrochemical laboratory with VoltaMaster 6 software.

Electrochemical studies of the processes occurring during the oxidation of niobium in a solution of phosphoric acid H_3PO_4 (0.28 M) were carried out using the method of cyclic voltammetry
Polarization measurements were carried out in a three-electrode electrochemical cell.

The morphology of the coatings was investigated using a “Tixomet” image analyzer on an Axio Observer.D1m microscope «Carl Zeiss». The roughness of niobium coatings was determined using a Taylor Hobson profilometer-profilograph.

3. Electrodeposition of niobium coatings

The electrodeposition of niobium coatings was carried out from a chloride-fluoride electrolyte of the composition NaCl-KCl-NaF (10 wt.%) - K_{2}NbF_{7} (8 wt.%). The cathodic current density was 15 mA/cm\(^2\), the temperature was 750 °C, and the cathode rotation speed was 30–40 rpm. The experimental procedure is described in detail [1].

Figure 1 shows the appearance of a spherical rotor before (figure 1a) and after electrodeposition coating (figure 1b) and the morphology of obtained coating (figure 1c).

![Figure 1](image)

**Figure 1.** External view of the spherical rotor before (a) and after electrodeposition coating (b); the melt NaCl-KCl-NaF(10 wt.%)-K_{2}NbF_{7}(8 wt.%), j = 15 mA/cm\(^2\), \(\tau\) = 8 h, \(t\) = 750°C; the morphology of obtained coating (c).

4. Electropolishing of niobium coatings

Since after the electrolytic deposition of the niobium coating its roughness corresponds to the 8-9 class of surface finishing, an additional two-stage treatment is required, including the processes of electrochemical and mechanical finishing.

To reduce the surface roughness the electrochemical polishing (EP) of the coating was carried out. Electropolishing is a process characterized by smoothing the metal surface to a mirror finishing by dissolving it anodically in an appropriate electrolyte solution. A rotor made of carbopyroceram with a niobium coating served as an anode, and a molybdenum plate served as a cathode.

The thickness of the initial niobium coating on a 10-mm-diameter carbopyroceram sphere was 127 μm. Five stages of electropolishing were performed with the duration of each stage of 2 minutes. From the analysis of the microstructure (figure 2), it was found that during electropolishing, the crystals of the coating are etched with leveling of the surface. In the course of research, it was determined that electropolishing should be carried out in stages at a potential of no more than 6 V.

After electropolishing the surface was machined with diamond pastes with a particle size of 1 to 0.3 μm. Upon completion of the polishing process (13-14 class of surface finishing), the surface was cleaned from the remains of abrasive materials in succession in distilled water and ethyl alcohol and dried in air at a room temperature.

5. Electrooxidation of niobium coatings

The cyclic voltammetric curve obtained in solution of H\(_3\)PO\(_4\) (0.28 M) on a niobium electrode is shown in figure 3.
Figure 2. Appearance and microstructure of the rotor before (a) and after (b) a series of electropolishing: EP1 (8 V, 2 min.), EP2 (6 V, 2 min.), EP3 (6 V, 2 min.), EP4 (6 V, 2 min.), EP5 (6 V, 2 min.).

The limiting stage of the anodic oxide formation on the niobium surface is the counter electrodiffusion of metal cations and oxygen anions under the action of an electric field in the volume of the growing film [4]. The reaching of the limiting current density value on the CV curve (figure 3) in the forward direction of potential sweep and the subsequent rise of the current density to a plateau is expressed by the high field mechanism of oxide film formation [5, 6].

Figure 3. Cyclic voltammetric curve. Electrolyte – H₃PO₄ (0.28M), working electrode – niobium, auxiliary electrode – molybdenum, reference electrode – silver chloride (4M KCl), scan rate – 0.1 V/s, working electrode area – 7,47·10⁻³ cm², temperature – 293 K.

Electrooxidation was carried out in an aqueous solution of 1% phosphoric acid with a stepwise increase in voltage from 30 to 90 V with a step of 30 V (table 1). A rotor with a niobium coating served as an anode, and a molybdenum plate served as a cathode. The rotation speed of the anode with the rotor was 30 rpm. The duration of each stage was controlled by the current flowing through the cell. As soon as the current became zero, the oxidation potential was increased. Figure 4 shows a scheme of a setup for the electrochemical oxidation of niobium.
Figure 4. Scheme of the setup for the electrochemical oxidation of niobium. 1 - Container with 1% H₃PO₄ solution, 2 - Rotating anode with rotor, 3 - Molybdenum cathode, 4 - Stirrer, 5 - Power supply B5-50.

### Table 1. Oxidation conditions.

| Anodization potential (V) | Anodization time (min) |
|---------------------------|------------------------|
| E₁ = 30                   | τ₁ = 10                |
| E₂ = 60                   | τ₂ = 5                 |
| E₃ = 90                   | τ₃ = 5                 |

6. Conclusion

Thus, the process of creating a superconducting niobium coating on a cryogyroscope rotor includes the following stages: deposition of a superconducting niobium coating on spherical substrates, electropolishing and mechanical finishing of obtained coatings and its subsequent electrooxidation.

References

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