Electrolytic superconducting niobium coatings for a cryogroscope rotor: creation and properties

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Abstract. Electrodeposition of niobium coatings on spherical substrates for a cryogroscope rotor made of carbopyroceram was considered. A special design of the installation for obtaining coatings on spherical samples was created. The coatings were applied at a temperature of 750 ºC with the cathodic current density of $5 \cdot 10^{-3} - 2 \cdot 10^{-2}$ A·cm$^{-2}$ and the electrolysis time of 8-12 h. It was found that the use of a cathodic current density of $2 \cdot 10^{-2}$ A·cm$^{-2}$ and higher is impractical, because there is a roughening of the coatings surface. The composition of electrolytic coatings was identified by XRD analysis. The macrostructure of niobium coatings was studied using electron microscopy. The concentration of metallic impurities in the niobium coatings was defined by spectral quantitative analysis. The content of gas impurities was determined by gas chromatography. The roughness, nonsphericity, and superconductive properties of niobium coatings were investigated.

1. Introduction
In study [1] it was found that the most promising substrate for a cryogroscope rotor is a carbopyroceram (CPC). The use of a rotor made from this material in a cryogroscope is possible if a superconducting coating is applied to the substrate. Niobium was used as a superconductor because it has a high critical temperature of the transition to the superconducting state in comparison with other elements. It can also be easily processed by mechanical, chemical and electrochemical methods.

There are many methods for obtaining niobium coatings. Electrolysis of molten salts is the most promising of them, because this method makes it possible to obtain uniform coatings, including articles of complex configuration. Since the rotor is a spherical sample with a diameter of 10 mm, a special design of a rotating cathode was created to accomplish this task. A rotating cathode consists of two molybdenum discs located horizontally and parallel to each other. The upper disc remains stationary and has an annular stop to prevent the sphere from falling, and the lower one is mounted on the vertical rotating shaft of the overhead stirrer. The sample moves between the discs, which makes it possible to obtain coatings uniform in thickness due to electrical contact at any point of the sphere.

For a better understanding of electrodeposition process, the electrochemistry of niobium on a carbopyroceram electrode was studied. The kinetic parameters (transfer coefficient and diffusion coefficient) of the electroreduction process Nb(IV) to Nb in an electrolyte of the composition NaCl-KCl-NaF (10 wt.%)-$K_2$NbF$_7$ in contact with a metallic niobium at a temperature 1023 K were obtained.
2. Experimental

A glassy carbon crucible SU-2000 brand was used as a container for the melt in the processes of electrodeposition, a spherical sample of carbopyroceram was used as a cathode, and a crucible lining made of niobium was an anode [2]. The conditions and electrolytic method for obtaining a superconducting niobium coating on the cryogyroscope rotors require the creation of a high-purity atmosphere of an inert gas (argon). The inert atmosphere in the cell was maintained using a pressure regulator and an inert gas reservoir. Electrochemical cell for obtaining niobium coatings on spheres is shown in figure 1.

![Electrochemical cell for obtaining niobium coatings on spheres](image)

**Figure 1.** Electrochemical cell for obtaining niobium coatings on spheres. 1 – retort, 2 – lid, 3 – glassy carbon crucible, 4 – holes with spigots, 5 – current lead, 6 – fixing rod, 7 – gasket system, 8 – anode, 9 – cathode, 10 – overhead stirrer, 11 – rotating disc electrode, 12 – retainer, 13 – sample, 14 – ring stop.

The electrodeposition of niobium coatings on spheres was carried out at a temperature of 1023 K. The cathodic current density during electrolysis varied in the range $5 \times 10^{-3} - 2 \times 10^{-2}$ A cm$^{-2}$, the rotation speed of the stirrer in all experiments did not change and was chosen equal to 35 rpm [3]. The electrolysis time was 8-12 h.

Such conditions made it possible to obtain coatings with the thickness up to 140 μm. It was found that the use of a cathodic current density of $2 \times 10^{-2}$ A cm$^{-2}$ and higher is impractical because there is a surface roughening of the coatings.

For identification of electrolytic coatings a Shimadzu XRD-6000 diffractometer was used. The macrostructure of niobium coatings was investigated using an Axio Observer.D1m electron microscope with a Thixomet image analyzer. The concentration of metallic impurities in the niobium coating was determined by spectral quantitative analysis on an Iskroline 300 instrument and after dissolution of the niobium coating using a Perkin Elmer AAS 4100-ZL atomic absorption spectrometer. The gases in niobium were detected by a Gas Chromatograph-Mass Spectrometer GCMS-QP 2010 Ultra Shimadzu. The roughness and nonsphericity of the samples were measured using a Taylor Hobson Talyrond 595 profilograph-profilometer. The superconducting properties of niobium coatings were determined by an AC-Magnetometer.
3. Results and discussion

The appearance of a carbopyroceram sample before (a) and after electrolysis (b) is shown in figure 2.

![Figure 2. Appearance of a carbopyroceram sample: (a) – initial; (b) – niobium-coated.](image)

Figure 2. Appearance of a carbopyroceram sample: (a) – initial; (b) – niobium-coated.

The surface of the niobium coating after electrodeposition corresponds to the 8-9 class of surface finishing. Superconducting properties depend on the surface roughness, therefore an electropolishing of a niobium coating is required after electrodeposition. Electropolishing was carried out in a mixture of H$_2$SO$_4$:HF (9:1) acids. This treatment allows to reduce the coating roughness.

The concentration of impurities in the niobium coating was analyzed by various methods. Spectral quantitative analysis of niobium coatings was used for detection of the following impurities (wt.%): Mn$<2\times10^{-4}$; Mg$<3\times10^{-4}$; Si$<1\times10^{-3}$; Fe$=2.3\times10^{-3}$; Ni$<5\times10^{-4}$; Pb$<5\times10^{-4}$; Sn$<5\times10^{-4}$; Ti$<1\times10^{-3}$; Al$<5\times10^{-4}$; Co$<1\times10^{-3}$; Mo$<1\times10^{-3}$; Ca$<1\times10^{-3}$; Zr$<2\times10^{-3}$; V$<3\times10^{-4}$; Cu $\leq 1\times10^{-3}$; Cr$<5\times10^{-4}$. Gas chromatography was utilized for the determination of oxygen and nitrogen (wt.%): O$_2$ = 0.01; N$_2$ < 0.001.

The roughness of obtained coatings was $R_a = 0.4$ μm and nonsphericity was $S_p = 0.2$ μm.

The superconducting properties of a rotor with electrolytic niobium coating on carbopyroceram were measured in comparison with a rotor made of all-metal niobium (grade “Nb1”).

The critical superconducting transition temperature and critical transition fields for the samples at different temperatures are presented in tables 1 and 2.

**Table 1.** Critical transition temperature of the sample at “zero field”.

| Samples | $T_{c}$, K | $\delta T_{c}$, K |
|---------|------------|------------------|
| Nb1     | 8.84       | 0.07             |
| CPC     | 8.36       | 0.08             |

**Table 2.** Critical transition fields of the sample at different temperatures.

| Temperature, K | $H_{c1}$, O$_e$ | $H_{c2}$, O$_e$ |
|---------------|----------------|----------------|
|               | Nb1            | CPC            | Nb1            | CPC            |
| 4.5           | 4.7            | 7.7            | 10             | ~ 12           |
| 5.0           | 4.0            | 6.2            | 8.2            | 9.5            |
| 5.5           | 3.5            | 5.0            | 7.0            | 8.0            |
| 6.0           | 2.8            | 4.0            | 6.0            | 6.2            |
| 6.5           | 2.2            | 3.0            | 4.6            | 4.5            |
| 7.0           | 1.6            | 2.0            | 3.5            | 3.0            |
| 8.0           | 0.6            | 0.4            | 1.5            | 0.8            |
From the data given in tables 1 and 2, it can be seen that the sample of all-metal niobium is inferior in superconducting characteristics to the sample of carbopyroceram with electrolytic niobium coating. Such characteristics make it possible to use a niobium coating on the carbopyroceram substrate in cryogenic devices.

The final stage in creating of superconducting coating is protection it from the environment because niobium has a high affinity for oxygen. Oxygen reduces the metal plasticity, effects on the electrical properties, increases the specific niobium resistance, and reduces the transition temperature to superconducting state. To eliminate the abovementioned disadvantages, a niobium pentoxide film was formed on the niobium coating. The protective film was obtained by the anodic oxidation in a 1% solution of phosphoric acid. The appearance of a niobium-coated carbopyroceram sample before (a) and after anodic oxidation (b) is shown in figure 3.

![Figure 3. Appearance of a niobium-coated carbopyroceram sample: (a) – initial; (b) – with a protective film.](image-url)

**4. Conclusions**

A special design of the installation for obtaining coatings on spherical samples by the electrolytic method was created, which makes it possible to obtain coatings uniform in thickness.

The niobium coatings in carbopyroceram spheres were obtained at 750 °C at the cathodic current density $5 \times 10^{-3} - 2 \times 10^{-2} \text{ A}\cdot\text{cm}^{-2}$ and the electrolysis time 8-12 h. The rotation speed of the stirrer in all experiments did not change and was chosen equal to 35 rpm. Such conditions made it possible to obtain coatings with the thickness up to 140 μm. It was found that the utilization of cathodic current density of $2 \times 10^{-2} \text{ A}\cdot\text{cm}^{-2}$ and higher is impractical because there is a surface roughening of the coatings.

After the electrodeposition the coatings were electropolished in a mixture of $\text{H}_2\text{SO}_4$:$\text{HF}$ (9:1) acids. This treatment allows to reduce the coating roughness. The treated coating was analyzed for the presence impurities by two methods: spectral quantitative analysis, gas chromatography. The roughness of the coatings and the sample nonsphericity were measured. The superconducting properties of a rotor with electrolytic niobium coating on carbopyroceram were measured in comparison with a rotor made of all-metal niobium.

To solve the problem of niobium protection from the environment a niobium pentoxide film was formed on the niobium coating by the anodic oxidation in a 1% solution of phosphoric acid.

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**References**

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