Electropolishing of niobium coatings on spherical shape samples

Yu V Stulov, A R Dubrovskii, M A Okunev, O V Makarova and S A Kuznetsov
Tananaev Institute of Chemistry of the Federal Research Centre “Kola Science Centre of the Russian Academy of Sciences”, Apatity, 184209, Russia

E-mail: stulov@chemy.kolasc.net.ru

Abstract. Selection of electropolishing parameters on rolled niobium samples (10×20 mm) in the mixed solution H₂SO₄ – HF was performed. The range of potentials and the duration of electropolishing were chosen. A special anode construction for the electropolishing of spherical shape samples from carbypyroceram coated niobium was used. Due to the small niobium coating thickness on the rotor, electropolishing was carried out in several stages. The duration of each stage was 2 minutes and totally five electropolishings were performed. It was found that the electropolishing of spherical shape samples should be carried out at a potential of 6.0 V relatively to the cathode from glassy carbon.

1. Introduction
Electrochemical polishing (EP) is an electrochemical process that removes material from a metallic work piece, reducing the surface roughness by levelling micro-peaks and valleys, improving the surface finishing. It is used to polish, passivate, and deburr metal parts. The important feature of the electropolishing process is its ability to dissolve asperities (peaks) on the work surface much faster than the material in “micro-valleys”. Such selective dissolution is a result of different values of the electrical potential of the peaks and valleys. The positive charge of the anodically connected work piece is concentrated in the peaks where the current density is higher than average, which causes a selective dissolution of the peaks and a smoothening of the surface.

The mechanism of this process is as follows, the work-piece is immersed in a temperature-controlled bath of electrolyte and serves as the anode; it is connected to the positive terminal of a DC power supply, the negative terminal being attached to the cathode. A current passes from the anode, where metal on the surface is oxidized and dissolved in the electrolyte, to the cathode. At the cathode, a reduction reaction occurs, which normally produces hydrogen.

The superconducting properties of niobium largely depend on the quality of its surface. One of the final stages of surface treatment is electropolishing. The electropolishing process of niobium is the subject of numerous studies performed by various authors [1–8]. Electrochemical polishing substantially depends on the viscosity and/or electrical resistivity of the electrolyte used. Various electrolyte compositions based on hydrofluoric, sulfuric, nitric and phosphoric acids taken in various concentrations are used [1–3, 6–8]. The dissolution of the oxide layer on a metal surface can be conducted by utilization hydrofluoric acid. Phosphoric, sulfuric and other acids form a viscous medium necessary for electrolytic polishing.
The study of the anodic treatment niobium process in a mixture of concentrated sulfuric and hydrofluoric acids [2, 3] showed that the effect of polishing is achieved under the conditions of the oxide film formation on a metal. Potentiostatic electrolysis is accompanied by current oscillation caused by the periodic formation and dissolution of Nb₂O₅ monolayers.

2. Experiment
Selection of electropolishing parameters was carried out on rolled niobium samples (10×20 mm) in the mixed solution H₂SO₄ – HF (9:1). The process was carried out by use an electrochemical cell in which niobium was the anode and a glassy-carbon crucible – the cathode. The selection of parameters was made empirically, taking into account the literature data [1–8]. The range of potentials was chosen from 8.0 to 15.0 V and the duration of electropolishing was from 30 to 60 minutes. The sample was kept for 5–10 minutes in the electrolyte at the end of the process to completely remove the oxide film.

For the electropolishing of carbopyroceram spherical-shaped samples 10 mm in diameter coated niobium was used a special anode construction. It consists of two parts: top part is fixed; bottom part is rotating by digital controlled stirrer. Construction of the anode provides the electrical contact in a random point of the sample. Due to such contact a uniform surface smoothing is occurred.

The morphology of samples was investigated using a “Tixomet” image analyzer on an Axio Observer.D1m microscope «Carl Zeiss». The roughness of niobium coatings was determined using a Profi-130 profilometer-profilograph.

Anodic polarization curves were obtained on a niobium electrode in the electrolyte H₂SO₄-HF (9:1) using the VoltaLab 40 dynamic electrochemical laboratory with VoltaMaster 4 software (version 6).

3. Results and discussion
A typical anodic polarization curve on niobium (figure 1) consists of the active dissolution of the metal (I) and the passivation area (II-IV) breaking down into formation sections of a viscous film at the anode of the niobium (II) dissolution, current oscillations (III) and sustained passivity (IV). The highest quality and rate of electropolishing are provided with anodic potentials φₙ–φₖ [7, 8]. Potential oscillations are unstable and sensitive to temperature changes and solution composition, size and parts configuration.

![Figure 1](image-url) **Figure 1.** Polarization curve of niobium anodic dissolution. Electrolyte – H₂SO₄-HF (9:1), working electrode – niobium, reference quasi-electrode – glassy carbon, auxiliary electrode – glassy carbon, polarization speed – 50 mV s⁻¹, working electrode area – 3 cm², temperature – 293 K.

Electropolishing of a rolled niobium at a potential of 15.0 V for 60 minutes led to a significant removal of the metal from the surface of the sample and a significant change in roughness was achieved. Figure 2 shows the surface morphology of the original sample (a) and after the first electropolishing (b).
The loss of sample mass was 0.05359 g cm\(^{-2}\), and the sample thickness decreased by 127 μm. In addition, with such voltage, the electrolyte is strongly heated and cooling is required to maintain a constant temperature. Therefore, at the next stage of the process, the potential and the process time were reduced to values of 12.0 V and 30 minutes, respectively.

When electropolishing a rolled niobium performed for 30 minutes at a potential of 12.0 V the removal of the metal was 0.0799 g cm\(^{-2}\) with a decrease in the sample thickness by 140 μm. The surface morphology of this sample is presented in figure 3a. Since the decrease in the sample thickness was 140 μm, it was decided to lower the process voltage to 8.0 V in order to achieve the desired coating removal value.

With further polishing of this sample at a potential of 8.0 V for 30 minutes the value \(R_a = 0.071\) μm was reached. Morphology is presented in figure 3b. A sample mass decrease was 0.0353 g cm\(^{-2}\), thickness decrease – 51 μm.

Niobium coatings up to 127 μm in the thickness were obtained by electrolysis from a melt of the composition KCl-NaCl-NaF(10 wt.%)-K\(_2\)NbF\(_7\)(8 wt.%) on the spherical samples, the substrates for which were carbopyroceram.

Since the coating thickness was this value, it was decided to conduct electropolishing of the spherical samples at potentials of not more than 8.0 V, in stages, in the electrolyte H\(_2\)SO\(_4\)-HF (9:1). The duration of each stage of electropolishing was 2 minutes. A total of 5 electropolishing was performed (EP\(_1\)–EP\(_5\)). During EP\(_1\) the current flowing through the cell reached (due to the large area of the rotating electrode) values of 10 A, which caused a strong heating of the electrolyte and intensive gassing. Therefore, the potential of electropolishing was subsequently reduced to 6.0 V. The general view and morphology of the initial spherical sample (SS) is presented in figure 4(a) [9], on figures

![Figure 2](image2.png)

**Figure 2.** Surface morphology of rolled niobium before (a) and after (b) electrochemical polishing. Process potential – 15.0 V, time – 60 minutes, temperature – 293 K.

![Figure 3](image3.png)

**Figure 3.** Surface morphology of rolled niobium after electrochemical polishing: (a) – process potential – 12.0 V, time – 30 minutes, temperature – 293 K; (b) – process potential – 8.0 V, time – 30 minutes, temperature – 293 K.
4(b)-(f) the image of SS after each stage of electropolishing. The results of mass and diameter changes of the SS are shown in table 1.

**Figure 4.** General view and morphology of spherical sample after electropolishing steps: (a) – initial rotor, (b) – EP₁ (8.0 V, 2 minutes), (c) – EP₂ (6.0 V, 2 minutes), (d) – EP₃ (6.0 V, 2 minutes), (e) – EP₄ (6.0 V, 2 minutes), (f) – EP₅ (6.0 V, 2 minutes).

**Table 1.** Changing the parameters of the SS during electropolishing.

| EP No. | SS diameter, mm | SS mass, g |
|--------|-----------------|------------|
| EP1    | 10.028          | 1.0759     |
| EP2    | 10.021          | 1.0669     |
| EP3    | 10.016          | 1.0604     |
| EP4    | 10.006          | 1.0533     |
| EP5    | 10.004          | 1.0476     |
|        | 9.993           | 1.0413     |
The mechanical processing traces are visible on the initial sample and after EP1 the cold-worked niobium layer on the initial sample was etch removal and the structure of electrolytic niobium is shown on the figure 4(b). Further electropolishing led to etching of coating crystals with surface leveling, the coating thickness decreasing was 35 microns per diameter.

4. Conclusion
Thus, the spherical samples should be electropolished stepwise in electrolyte H$_2$SO$_4$-HF (9:1) at a potential of 6.0 V relatively to the cathode from glassy carbon. The duration of each stage should be selected based on the coating etching rate, which for the abovementioned conditions was 3.5 μm min$^{-1}$.

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