Corrosion resistance of the substrates for the cryogenic gyroscope and electrodeposition of the superconductive niobium coatings

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Abstract. The interaction of different materials with the niobium containing melt was investigated. As substrate materials the ceramics, beryllium and carbopyroceram were chosen. Several spherical ceramic and beryllium samples were coated with protective molybdenum and niobium films by magnetron sputtering and PVD, respectively. After the experiment (exposition time 10 min) the exfoliation of molybdenum film from ceramic samples was observed due to interaction of the substrate with the melt. The niobium protective coatings reacted with the melt with niobium oxide formation. The beryllium samples regardless of the shape and the presence of the protective films were dissolved in the niobium containing melt due to more negative electrode potential comparing with niobium one. The carbopyroceram samples were exposed in the melt during 3 and 12 h. It was found that the carbopyroceram not corrodes in the niobium containing melt. The optimal regimes for electrodeposition of smooth uniform niobium coatings with the thickness up to 50 µm on carbopyroceram spheres were found.

1. Introduction

Niobium in the form of thin films and coatings is used in high-tech cryogenic devices using the phenomenon of superconductivity [1, 2]. For their preparation, the niobium ability can be used to form electrolytic structurally dense cathodic films in molten salts [3]. Electrolytic method does not require complex equipment and allows forming uniform coatings with the desired thickness on the inner and outer surfaces of articles with complex configuration. In this context, it is interesting to study the electrolytic niobium coatings on the different materials substrates, for their utilization in superconducting devices for various applications.

The ceramics, beryllium and carbopyroceram (CPC) are potential materials for the substrates.

Ceramics has the following advantages: retention of mechanical properties at high temperatures, high wear-resistance. The drawbacks included the following: a relatively high specific gravity, lack of conductivity and ductility, high hardness, susceptibility to cracking.

Beryllium has a low specific gravity and its disadvantages are a large anisotropy and thermal expansion coefficient, which is almost three times higher than that of niobium. In addition, beryllium is highly toxic and requiring special conditions for ensuring its handling.

Carbopyroceram is isotropic, gas-tight, solid and durable corrosion-resistant material that combines the properties of graphite and metal, able to withstanding repeated rapid heating followed by rapid cooling [4, 5].
There are many methods of niobium coatings deposition. One of the promising methods for deposition of superconductive (SC) niobium coatings is the electrolysis in molten salts, allows obtaining uniform coatings on articles with complex configuration. The electrolyte for electrodeposition of niobium is an aggressive media, so it is necessary to investigate the behavior of the substrate material in contact with the melt.

2. Experimental

In this work, we used chloride-fluoride electrolyte with the composition NaCl-KCl-NaF(10 wt. %)-K2NbF7 (8 wt. %) [6].

As substrate materials the ceramic, beryllium and carbopyroceram of different shape (spheres, cylinders, parallelepipeds) for corrosion resistance studies were used. The time of the experiments was varied from 10 min to 12 h.

The current density and time of electrolysis for electrodeposition of smooth uniform niobium coatings were varied from $1 \times 10^{-1}$ to $2 \times 10^{-1}$ A cm$^{-2}$ and from 8 to 12 h, respectively. All experiments were conducted in an inert atmosphere of argon and the temperature was fixed at 750 °C.

3. Corrosion resistance studies

Since ceramics (Al2O3) is not conductive material prior to the experiment, the samples were coated by molybdenum and niobium using magnetron sputtering and PVD, respectively.

Examination of the sample (sphere with diameter 10 mm) showed that the poreless coatings cannot be obtained by magnetron sputtering and pore area (substrate surface non-coated by molybdenum) is on average 200 μm$^2$ (figure 1).

![Figure 1](image1.png)

**Figure 1.** Macro- (a) and microstructure (b) of ceramic sample with molybdenum protective coating before the experiment. Film thickness is approx. 1 μm.

Investigation of the sample surface after the experiment revealed that an average pore area increased by 27 times (figure 2) and XRD captures the formation of the niobium oxides of various compositions (NbO, Nb4O5, NbO2). To explain this result, the molybdenum corrosion behavior was studied in the same melt. Molybdenum plate (Aldrich 99.9+ %) kept standing for eight hours in the melt then was washed, weighed and analyzed by XRD. Sample weight and the diffraction pattern changes were not observed, indicating the high corrosion resistance of molybdenum in the niobium containing melt.

Niobium oxides are formed between the Al2O3 substrate and molybdenum coating during growth provide the mechanical impact on the coating, resulting in its exfoliation [7].

Spherical-shaped ceramics samples coated with niobium by PVD were tested under the same conditions. According to optical microscopy, niobium protective coatings were solid, smooth, mat-gray in color and without obvious defects prior to the experiment. Figure 3(a) shows the diffractogram of the sample prior to corrosion testing, which contains poorly formed peaks. Such distortions in the form of broadened lines can be a consequence of either very small crystal sizes or a change in the unit cell parameters due to interstitial impurities. The identification of all reflections is not possible, but
with a high probability it can be stated the following compounds: (▼) Nb₆O and (★) γ-Al₂O₃. Some of the peaks (+) can be related to compounds of niobium with light elements (H₂, N₂, O₂), and some peaks remain unidentified. After the corrosion tests, the increasing of the γ-Al₂O₃ peaks intensity is recorded, indicating a thinning of the protective coating and its interaction with the melt leads to the formation of the NbO₂ compound (figure 3(b)).

Figure 2. Macro- (a) and microstructure (b) of ceramic sample with molybdenum protective coating after the experiment. Conditions: NaCl-KCl-NaF(10 wt. %)-K₂NbF₇(8 wt. %) melt in contact with Nb, τ = 10 min, T = 750 °C.

Figure 3. The XRD data of the sample with niobium protective coating of before (a) and after (b) corrosion resistance tests.

Spherical and cylindrical beryllium samples with molybdenum coating and without it were tested at the same conditions as samples from ceramics. It was found that dissolution of the substrate occurs at a high speed because its electrode potential is more negative than niobium. Figure 4 shows the image of beryllium cylindrical sample surface. Evident that at the sample surface before the testing clearly expressed by machining grooves (figure 4(a)). After the test, the surface becomes a characteristic of the material subjected to dissolution (figure 4(b)).

Carbopyroceram samples were exposure in niobium containing melt for 3 and 12 h at a temperature of 750 °C. After a three-hour exposure in the melt XRD pattern of the sample remains the same, but after 12 h exposure XRD pattern shows the formation of niobium carbide layer (NbC) on the carbopyroceram surface.

Thus, magnetron sputtering and PVD methods could not provide the efficient metal protection coatings to apply it in molten salt media. Based on the corrosion tests, the carbopyroceram as a substrate for the electrodeposition of niobium coating was selected.
Figure 4. The microstructure of the beryllium cylinder side surface before (a) and after (b) the experiment. Conditions: NaCl-KCl-NaF(10 wt. %)-K$_2$NbF$_7$(8 wt. %) melt, $\tau = 10$ min, $T = 750$ °C.

4. Electrodeposition of niobium coatings

Electrodeposition of the niobium coatings on spheres 10 mm in diameter, manufactured of carbopyroceram, carried out at a temperature of 750 °C. The anodic current density was less than $10^{-3}$ A cm$^{-2}$ and the cathodic current density during electrolysis was chosen $2 \cdot 10^{-1}$ A cm$^{-2}$. The NaCl-KCl-NaF(10 wt. %)-K$_2$NbF$_7$(8 wt. %) electrolyte was used for niobium coatings electrodeposition on carbopyroceram spheres. Due a spherical shape of substrates, a special form of the cathode should be used for plating of samples by niobium in molten salts. In the present study the construction of the cathode was developed. It consists of two parts: top part is fixed; bottom part is rotating by digital controlled stirrer. Construction of the cathode provides the electrical contact in a random point of the sample. Due to such contact a uniform coatings can be obtained. The stirrer rotation speed in all experiments was not changed and was chosen to be 30 rpm. Electrolysis time was chosen 8 h to obtain smooth uniform niobium coatings with the thickness 50 µm (figure 5).

Figure 5. External view (a) and specimen surface morphology (b) of the carbopyroceram sample coated by niobium. Conditions: NaCl-KCl-NaF(10 wt. %)-K$_2$NbF$_7$(8 wt. %) melt, $\tau = 8$ h, $T = 750$ °C.

Spectral quantitative analysis of niobium coatings detected the following contents of impurities (wt. %): Mn < $2 \cdot 10^{-4}$; Mg < $3 \cdot 10^{-4}$; Si < $10^{-3}$; Fe = $2.3 \cdot 10^{-3}$; Ni < $5 \cdot 10^{-4}$; Pb < $5 \cdot 10^{-4}$; Sn < $5 \cdot 10^{-4}$; Ti < $10^{-3}$; Al < $5 \cdot 10^{-3}$; Co < $10^{-3}$; Mo < $10^{-3}$; Ca < $10^{-3}$; Zr < $2 \cdot 10^{-3}$; V < $3 \cdot 10^{-4}$; Cu < $10^{-3}$; Cr < $5 \cdot 10^{-4}$.

Testing of the samples on the superconducting properties showed the same results as the samples of whole niobium of high purity.

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