Niobium-niobium oxide multilayer coatings for corrosion protection of Havar®.

H. Skliarova1,2*, O. Azzolini1, M. Renzelli1, E. Bemporad3, R. R. Johnson4, V. Palmieri1,5

1 National Institute of Nuclear Physics, Legnaro National Laboratories, Viale dell'Università, 2 – 35020 Legnaro (Padua), Italy.
2 University of Ferrara, Ferrara, Italy
3 University of Rome "Roma TRE", Via della Vasca Navale 79 - 00146 Rome, Italy.
4 BEST Cyclotron Systems Inc., 8765 Ash Street Unit 7, Vancouver BC V6P 6T3, Canada.
5 University of Padua, Padua, Italy

INTRODUCTION

Chemically inert coatings on Havar® entrance foils of the targets for [18F] production via proton irradiation of enriched water at pressurized conditions are needed to decrease the amount of ionic contaminants released from Havar®. During current investigation, magnetron sputtered niobium and niobium oxide were chosen as the candidates for protective coatings because of their superior chemical resistance. Aluminated quartz substrates allowed us to verify the protection efficiency of the desirable coatings as diffusion barriers. Two modeling corrosion tests based on the extreme susceptibility of aluminum to liquid gallium and acid corrosion were applied. As far as niobium coatings obtained by magnetron sputtering are columnar, the grain boundaries provide a fast diffusion paths for active species of corrosive media to penetrate and to corrode the substrate. Amorphous niobium oxide films obtained by reactive magnetron sputtering showed superior barrier properties according to the corrosion tests performed. In order to prevent degrading of brittle niobium oxide at high pressures, multilayers combining high ductility of niobium with superior diffusion barrier efficiency of niobium oxide were proposed. The intercalation of niobium oxide interlayers was proved to interrupt the columnar grain growth of niobium during sputtering, that should result in improved diffusion barrier efficiency of obtained multilayers.

EXPERIMENTAL DETAILS

The coatings were deposited by DC sputtering with a 2 inches in diameter planar magnetron source in a cylindrical 316 L stainless steel vacuum chamber of 11 cm diameter and 26 cm in length. The substrates were placed onto a planar substrate holder at 6 cm from the cathode. Before sputtering, the chamber was pumped to a base pressure of 3·10⁻⁴ Pa by a Pfeiffer turbo molecular pump of 360 l/min and a primary pump Varian Tri Scroll Pump of 12 m³/hr.

The investigation of optimal parameters for sputtering of niobium oxide for sufficient deposition rate of stoichiometric niobium oxide by reactive sputtering was described in previous work [1]. Reactive sputtering of stoichiometric Niobium oxide was performed at 1 Pa total sputtering gas pressure using 3 sccm of Ar and 7 sccm of O₂ and 0.5 A DC. The value of deposition rate for the niobium oxide by reactive sputtering 0.2 nm/sec was used for the estimation of the thickness of niobium oxide layer in multilayers (see Table 1).

The multilayer architecture was shown to influence the mechanical stability of multilayer [2-4]. Thus, multilayer samples with different periodicity, were prepared by fixing the argon flux at 3 sccm, and periodically switching the oxygen flux from 0 sccm to 7 sccm. The deposition parameters used are resumed in Table 1. We have investigated two different architectures, preparing coatings made by 30 thin layers (M1) and by 6 thick layers (M2). In both cases, the Nb₂O₅ thickness was always intended to be ten times thinner than Nb (see Table 1). In order to perform reliable multilayer depositions, the oxygen flux was controlled with appropriate automated feedback. The coating with thick layers was prepared also by thermal oxidation of Nb layer introducing the maximum oxygen flux, immediately after each layer deposition (M3).
MULTILAYER ANALYSIS

The SEM picture in Fig. 1(a) displays the multilayer section of the 30 thin layers of the M1 coating. It allows to estimate an average bi-layer (layer of Nb + layer of Nb₂O₅) thickness of about 70 nm. From the Fig. 1(b) the thickness of the Nb and the Nb₂O₅ layers in the M2 coating was estimated about 260 nm and 160 nm correspondingly. The Fig. 1(c) shows the clear multilayer structure of the M3 coating with the layer thickness of about 220-280 nm.

The average grain sizes for M2 and M3 are represented in the Table 2.

The XRD patterns of the multilayer coatings are presented in Fig. 2. The XRD patterns of multilayer coatings with thick Nb layers architecture (M2 and M3) were found quite similar to the one of pure Nb coating.

Otherwise the thin layers multilayer pattern (M1) showed significant peak broadening proving the crystallite size decrease. The cubic lattice parameters and the average crystallite sizes for the investigated coatings obtained from the XRD data are presented in Table 2.

The decrease of each bi-layer thickness resulted in a significant decreasing of the average crystallite size of niobium (see Table 2), passing from 16 nm for the sample M2 and 18 nm for the M3 to 5 nm for the M1 sample. The XRD investigation was carried out by performing the θ-2θ Goniometer scan in Bragg-Brentano configuration with 2θ from 10° to 100° (180°-2θ is the angle between the X-ray source, the substrate and the detector). The 1.54 Å Cu-Kα X-ray was used to observe X-ray diffraction of thin films with a Panalytical (ex-Philips) PW3040/60 Diffractometer.

CONCLUSIONS

The use of an appropriate multilayer architecture was found sufficient to combine the properties of the niobium and the niobium oxide layers with the aim to reach a high diffusion barrier efficiency and high thermal stability. The intercalation of the Nb₂O₅ interlayers was proved to interrupt the columnar grain growth of Nb during sputtering, that should result in an improved diffusion barrier efficiency. For the thick layer multilayers the grain size of Nb in the crystalline metallic layer was found to increase with the layer thickness, however the crystallite size was similar to the one of the pure niobium coating.

The decrease of the bi-layer thickness from 280 nm to 70 nm resulted in the decrease of the grain size and the average crystallite size of Nb layer.

---

Table 2. Microstructure and barrier properties

<table>
<thead>
<tr>
<th>Sample n°</th>
<th>Nb</th>
<th>Nb₂O₅</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method</td>
<td>Sputtering</td>
<td>Reactive sputtering</td>
<td>Fine layers</td>
<td>Thick layers</td>
<td>Thermal oxidation</td>
</tr>
<tr>
<td>Average crystallite size (XRD), nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>amorphous</td>
<td>5</td>
<td>16</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Average grain size (SEM), nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>amorphous</td>
<td>-</td>
<td>70</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Cubic lattice parameter, Å</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---