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Niobium oxide thin layers characterized by Raman spectrocopy and SEM-FIB

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Abstract

Niobium is known as an alloying element for steels and its anodic oxide thin films are useful to technological applications, for example, capacitors, electrochromic devices, solar cells and biocompatible interfaces. In this study, two kinds of thin oxide niobium layers green and pink from National and European (reference) samples were characterized by Raman spectroscopy and by SEM-FIB transversal sections cuts to compare both of them due to differences of mechanical behavior observed during industrial processing among green and pink niobium oxide coatings.

Keywords: Anodization; Niobium.

Introduction

Niobium is widely used as an alloying element for improving microstructure, properties and performance of steels [1]. Anodic oxide thin films have been studied due to their technological applications as a material for capacitors, electrochromic devices, solar cells and biocompatible interfaces [2]. These thin film characteristics depend on the electrolyte and the applied voltage used to produce the layers during the anodization process [2,3]. Komatsu et al. report a linear correlation between applied voltage and film thickness of the anodic layers obtained in a citric acid solution. Anodic oxide thin layer color has changed according to voltage applied and the thickness of these layers is around hundreds of nanometers [3]. The process of anodized niobium products has developed, and it was verified different mechanical behaviors among two colors of anodized niobium samples during the industrial processing. The aim of this study was to characterize two kinds of thin oxide niobium layers: the first one obtained by anodization of niobium samples in phosphate salt solution, called National sample; and the second, anodized niobium samples from European (reference material). Both of them were made in two colors: green and pink oxide layers. For this, Raman Spectroscopy was employed to chemical qualitative identification and Ion Focused Bean Microscopy (FIB) to cut and to measure the thickness of the films. These surface techniques were important in this situation because the layers' thicknesses were in nanometers order and the classical metallographic analysis damaged the oxide layers during the cutting process.

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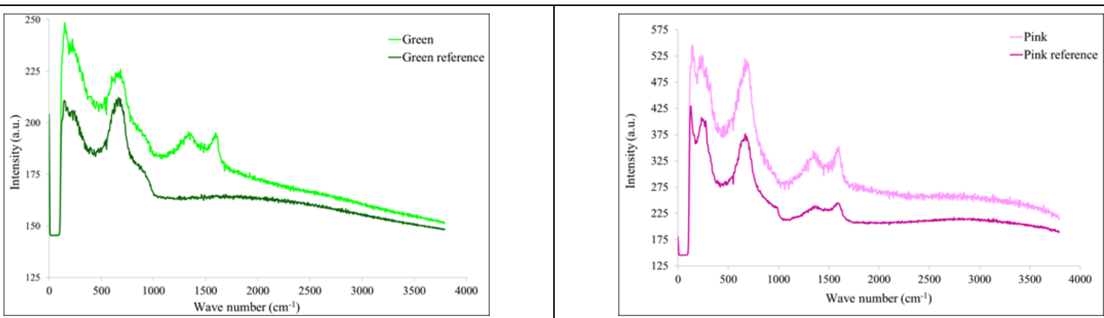
Methodology

Raman Witec microscope, model alpha 500, was employed during this study to identify crystalline or amorphous phases of the oxide layers. The 532 nm laser was chosen and the laser power was kept below 20 mW. Each spectrum corresponds to the average of 100 accumulations acquired with integration time of 50 s.
FEI Focus Ion Beam (FIB) scanning electronic microscope, model Quanta 400, was used to cut and to measure de oxide layers.

Results and discussion

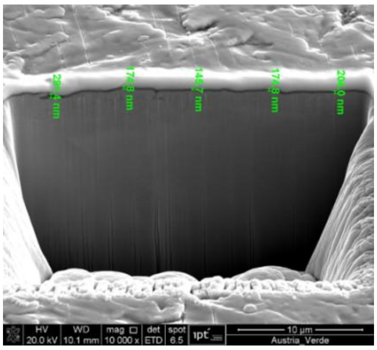
Figures 1 presents the Raman spectra of the National and the reference sample.



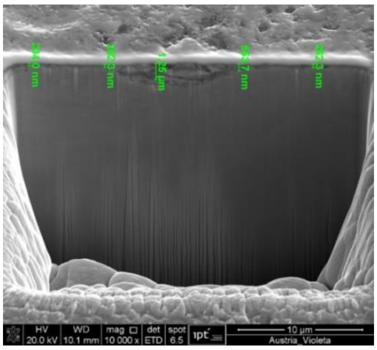
(a) (b)

Figure 1 – Raman spectra of anodized Nb surfaces: (a) green for National sample; green reference to European material; (b) pink for National sample; pink reference to European material.

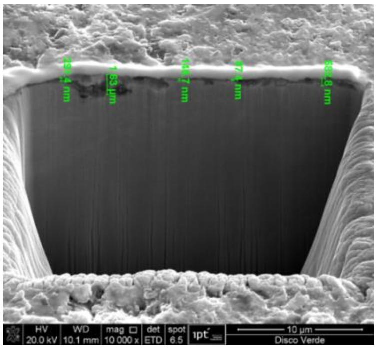
The band at 680 cm^{-1} is assigned to NbO_2 by the literature [2]. The obtained spectra presented bands at 671 cm^{-1}, indicating the presence of NbO_2. It can be seen that the bands obtained for the anodized National and the European samples are similar to each other, Figures 1.
The literature attributed the bands at 1340 cm^{-1} and at 1600 cm^{-1} to the amorphous carbon presence [4, 5]. The National samples showed bands of amorphous carbon more intense than the European samples analyzed. Figure 2 shows the transversal sections made by FIB on the National and European surfaces samples.



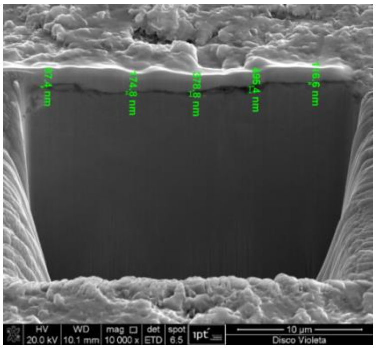
(a) Green reference



(b) Pink reference



(c) Green



(d) Pink

Figure 2 – Transversal sections made by FIB: (a) and (b) European samples (reference); (c) and (d) National samples.

The thickness measurements by SEM-FIB showed that all the anodized layers studied presented great thickness fluctuation, Table 1. The European green layer presented thicknesses ranging between 145.7 nm and 291.4 nm and the European pink layer presented thicknesses between 204.0 nm and 553.7 nm. The National green layer presented thicknesses between 87.4 nm and 291.4 nm and the National pink layer between 87.4 nm and 495.4 nm, Table 1.

Table 1 – Thickness values from European (reference) and National anodized layers by FEG-FIB analysis.

Identification	Thickness values(nm)				
	1	**2**	**3**	**4**	**5**
Green reference	291.4	174.8	145.7	174.8	196.7
Pink reference	204.0	262.3	1250.0*	553.7	340.0
Green	291.4	1630.0*	145.0	87.4	174.6
Pink	87.4	174.8	378.8	495.4	233.1

*Values do not consider due to anodized layer defects.

Conclusions

Raman spectroscopy and SEM-FIB techniques were important for phase characterization and thickness determination of Nb oxide thin films, respectively. The Raman spectra showed the bands obtained for National and European samples (green and pink) are similar to each other, with chemical composition attributed to NbO_2. Raman spectra indicated the presence of amorphous carbon on the surface of National samples preferably. The thicknesses for both samples, National and European, presented great value fluctuation.

References

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