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Evaluation of the resistance to oxidation of niobium treated by high temperature nitrogen Plasma Based Ion Implantation

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ABSTRACT

Niobium is a technological material used in very distinct applications. Most of them as an alloying element, making part of superconducting radio frequency cavities, nuclear reactor components, missiles, rockets, aviation and space-system engineering. Nevertheless, although refractory, pure niobium presents as the main drawback the poor oxidation resistance in moderate and high temperatures. Different treatment methods have been used to mitigate this issue, as is the case of cementation, conventional nitridation, CVD and PVD processes. The evaluation of the resistance to oxidation of Nb treated by high temperature nitrogen plasma based ion implantation (HTPBII) has been described herein. The implanted nitrogen in this case easily diffuses to inner layers of niobium heated up to 1250 °C during treatment, reaching depths of about 7 μm, while its atomic concentration of about 25% remains stable for almost the whole treated surface. This allows the formation of thick nitride layers. The produced interstitial nitrides have outstanding properties as the high hardness and strength, like ceramics, and high thermal and electrical conductivities, like metals. In addition, these refractory nitrides also present good chemical resistance and superior resistance against oxidation. The investigation performed herein includes a series of characterization performed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), glow discharge optical emission spectroscopy (GDOES), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The oxidation of the ion-implanted niobium was retarded in comparison with the untreated counterpart in about 130 °C. Isothermal analysis revealed reduced oxidation rate when treatment time was extended from 4 h to 8 h.

1. Introduction

Niobium and its alloys have been in the focus of regular investigation for many years, mainly due to their prominent properties and application in a variety of technological areas. Indeed, the pure metal holds a peculiar combination of chemical, mechanical and physical properties. It is ductile and tough, presenting high corrosion resistance, high strength at elevated temperatures, high melting point, high thermal conductivity and high coefficient of linear thermal expansion [1–2]. In addition, it exhibits the lowest density among refractory metals and low ductile-brittle transition temperature (DBTT) [3].

Nevertheless, in general, raw niobium is used as matrix-base alloys. Excepting the cases where application depends only on physical or chemical properties, alloyed material comes into consideration. The main problem regards its poor oxidation resistance at elevated temperatures [4], since oxygen diffuses freely through the metal in this case, causing embrittlement [5].

The alloying of niobium with other elements is a procedure commonly used to significantly improve its resistance against oxidation, by the addition of substitutional solutes (Mo, W, V, Ta), reactive elements (Zr, Hf, Ti) or interstitial nitrides and carbides (N,C) [6]. For high-temperature applications however, most of these elements cause some degradation to Nb properties. The DBTT can have substantial elevation with the insertion of solutes [6]. This is the case of Mo and W, even though both are effective strengtheners. On the other hand, Ti additions generate ductile alloys but at a cost of strength degradation. Vanadium is known to sharply degrade creep behavior and, as Ti, leads to severe melting point depression [7]. The increase of the alloy density is another drawback caused by all of these elements. As a consequence, other alternatives applied to face the problem of the poor high-temperature oxidation resistance of niobium lies in coatings.

It must be considered for these situations that the coating processes based on CVD and pack cementation lead to the increase of the DBTT and the worse of the mechanical properties. Even for coatings based on PVD, lower strength and ductility have been observed. For PVD, workpieces with sharp edges cannot be treated due to coating requirements. Another question to be raised is concerned with the adherence of the deposited film, which must be extremely high when the material

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is to be used in harsh environments and/or severe stress, as in aerospace applications.

In this paper pure niobium was treated by high-temperature nitrogen plasma based ion implantation, a non-line-of-sight treatment method, able to modify inner layers of the metal by nitrogen implantation. The association of the implantation with the elevation of the temperature of the substrate during treatment is important to promote the diffusion of the implanted nitrogen ions, in order to attain relatively thick modified layers. For refractory metals, as niobium, high temperature is essential to the formation of nitrides, with very interesting features [8,9]. In fact, NbN possesses good mechanical properties, such as hardness and toughness, high electrical and thermal conductivities, high melting point and superior tribological properties. Additionally, NbN plays the role of a protective layer against oxidation of the bulk metal.

The evaluation of the resistance to oxidation of Nb treated by HTPBII, not yet described in the literature, is the aim of this work.

2. Experimental

Raw niobium (99.7% purity), delivered by CBMM (Brazilian Company of Metallurgy and Mining), was cut in discs with 13 mm in diameter and 3 mm in thickness. These samples were polished to a mirror-like finish and cleaned before treatments in ultra-sound bath with acetone for 10 min and in isopropyl alcohol afterwards for other 10 min.

N-HTPBII was performed at a working pressure of 0.8 Pa. High negative voltage pulses of 7 kV/30 μs/500 Hz were applied to the workpieces for 4 h. For all cases the substrates were heated up to 1250 °C during treatments. Temperature of the substrates was measured by optical pyrometer. The heating is provided by the bombardment of electrons during H.V. pulse off-time. The experimental apparatus and a detailed explanation about the process can be found elsewhere [10, 11]. The substrate temperature during implantation was set based on previous experimental results [12] in which an enriched nitrogen layer of about 4 μm in depth was attained for Nb treated by N-PBII for only 1 h.

The phase composition of the treated samples was analyzed by X-ray diffraction (XRD), performed with Philips 3410 diffractometer in a standard theta-2theta Bragg–Brentano configuration with Ni-filtered Cu Kα radiation. The elemental depth profiles of the modified layers of niobium were obtained by glow discharge optical emission spectroscopy (GDOES) with averaged sputtering rates of 4.35 μm/min for Nb and of 3.45 μm/min for nitride zone. Respective profiles were attained with the help of a Jobin-Yvon GD profiler. Qualitative elemental analysis was attained by X-ray photoelectron spectroscopy (XPS), performed with a Kratos XSAM 800 spectrometer using Mg $K\alpha_{1,2}$ radiation and fixed analyzer transmission mode (80 and 40 eV pass energies for survey and detailed spectra, respectively). The spectra were referenced to the C 1s line (binding energy, BE = 285.0 eV) of the adventitious hydrocarbon type carbon. Data acquisition and processing were performed with the Kratos Vision 2 program [13]. The evolution of the spectra of the characteristic photoelectron peaks and the various chemical states of Nb were attained by Ar^+ etch profiling using XPS (Kratos MacroBeam ion gun). The pressure in the sample analysis chamber monitored by a trigger Penning gauge was 8×10^{-5} Pa. Ion energy of 2.5 keV and emission current of 15 mA were applied. The ion beam of about 2 mm spot size was rastered over the area of the sample, giving a current density related to the overall rastered area of about 1×10^{-5} A/cm^2. Three consecutive sputtering steps were applied, with durations of 30, 30 and 60 min. The surface morphology was examined by scanning electron microscopy (SEM) equipped with a Field Emission Gun (FEG) – Mira 3 – TESCAN, with a maximum magnification of 1,000,000. Finally, thermogravimetric analysis (TGA) was carried out in air up to 1100 °C using a NETZSCH Thermal Analyzer STA 449 F3 Jupiter equipped with simultaneous thermogravimetry and differential scanning calorimetry analyzes, that allows the measurement of mass changes and thermal effects between −150 °C and 2400 °C. The increase of the temperature with simultaneous measurement of the mass change was done in a constant step of 10 °C/min.

3. Results and discussion

The phase composition of the treated sample was analyzed by XRD, as can be seen by the proper diffractogram shown in Fig. 1. The evident presence of distinguished phases of niobium nitrides is clear. In fact, NbN (JCPDS 20-0801), Nb_2N (JCPDS 01-075-0952) and Nb_4N_3 (JCPDS 01-089-5131) peaks could be identified. The difference of XRD patterns between unimplanted and ion-implanted samples is a consequence of high enough thickness of the modified layers achieved in the current experiment since the nitride peaks could be detected by XRD performed with normal angle of incidence. Besides, it was observed the presence of niobium oxynitride Nb_2N0,88O0,12 (JCPDS 53-1025). It must be considered that oxygen is an impurity hard to be removed from vacuum chamber, even after vacuum conditioning. The high temperature of the substrate during treatment is another facilitator for oxygen diffusion. In fact, the ease with which oxygen diffuses through niobium, the strong Nb—O binding and considerable oxygen solid solubility [14] can explain the presence of niobium oxynitride in the diffractogram. Both, the niobium oxide and the oxynitride seem to form in the outermost layer, in accordance with GDOES analysis shown below.

XPS studies on as-received N PBII-treated Nb sample were performed to investigate the elements present on the surface and innermost regions upon Ar-ion sputtering, as shown in Fig. 2, revealing the quantitative changes. According to the results of quantification, there is a relatively high amount of carbonaceous surface contamination (about 47 at.%). In addition, there are 6 at.% Nb, 11 at.% N and 33 at.% O at the surface. C-content decreased after the first two etching steps (30 min + 30 min), from 47 to 33 and then to 20 at.%. An additional etching (+60 min) did not change essentially the surface C-content. O-content decreased after the first two etching steps, from 33 to 21 and then to 15 at.%. Increase of N-content was observed after the first two etching steps, from 11 to 19 and then to 27 at.%. In the same way, increase of Nb-content was observed after the first two etching steps, from 6 to 27 and then to 38 at.%.

The chemical bonds of O 1s, N 1s, C 1s and Nb 3d peaks detected on the surface are depicted in Fig. 3. Each peak is complex, suggesting the presence of more chemical states for the mentioned elements. The O 1s peak can be decomposed to three components at 529.9, 531.6 and 533.1 eV, assignable respectively to O in Nb_2O_5 and NbON, in oxidized carbon [15] or in OHδ-species [16], as shown in Fig. 3a. In Fig. 3b it can be seen that the N 1s peak has at least two components at 396.8 and 399.9 eV. That at lower binding energy (BE) can be assigned to oxynitride and nitride states, while that at higher BE to nitrogen, incorporated essentially in the grain boundaries [16]. In Fig. 3c, the C 1s peak reflects the presence of mainly hydrocarbon type surface contamination (BE = 285 eV). This peak has a shoulder on its high BE side, testifying to the presence of C bound to O and N. The complex Nb 3d peak can be decomposed to at least 3 doublets, as shown in Fig. 3d. The Nb $3d_{5/2}$ peaks at 203.9, 205.6 and 207.1 eV (and their respective $3d_{3/2}$ components, with a separation of about 2.7 eV towards the high BE side) can be assigned respectively to NbN, Nb oxynitrides and Nb_2O_5 [17]. Judging by the relative intensities of components in Fig. 3d, Nb is present mainly in nitride and oxide states at the surface, but oxynitrides can be also detected.

The evolution of the spectra of the characteristic photoelectron peaks upon Ar-ion etch is shown in Figs. 4a–c (Bottom spectra: untreated sample. Upper spectra in upward direction: samples Ar-ion etched for 30 min, 60 min and 120 min). Fig. 4a shows that the relative intensity of the shoulder of the C 1s peak (which reflects bonding of C to O and N) decreases. At the same time, a new component develops on the low BE side of the C 1s peak, assignable most likely to carbide