STRUCTURE AND NANOMECHANICAL PROPERTIES OF NbC AND NbCN COATINGS OBTAINED BY CATHODIC-ARC DEPOSITION WITH PULSED BIASING

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Abstract: Comparative studies of niobium carbide and niobium carbonitride coatings deposited on AISI 430 stainless steel have been presented. The NbC and NbCN coatings have been deposited by vacuum-arc evaporation in Bulat type device by using pulsed biasing mode with repetition frequency 50 kHz. It was demonstrated that pulsed biasing resulted in decreasing the micro-arcs formation. The obtained results show that plasma based PVD deposition in biasing mode could be rather prospective for novel medical applications, including coatings for stomatology.

1. Introduction

Transition metals as tantalum and niobium are excellent candidates as biocompatible coatings for various medical applications including dental implants [1]. Nb has lower melting point, lower density and greater availability and therefore has lower cost in comparison with Ta. Applications of Nb as a metal or as an alloying addition can be found in cathodic protection systems, heat exchangers, electronic components, superconductors, cutting and grinding tools, nuclear industry and more [2, 3].

Techniques such as chemical vapor deposition (CVD) and physical vapor deposition (PVD) allow applying Nb, NbC, NbN and Nb_2O_5 of a huge variety of materials with different composition and microstructure [4]. Mostly Nb based coatings have been applied by using DC or RF magnetron sputtering [5, 6]. But there is lack of data considering vacuum-arc evaporation techniques to produce niobium carbide and niobium carbonitride coatings.

In this paper, The NbC and NbCN coatings have been deposited by vacuum-arc evaporation in Bulat type device by using pulsed biasing mode. The structure, chemical composition and mechanical properties have been evaluated in order to modulate the coatings behavior on dental implants material made of stainless steel. The surface modification by thin film technology can improve interaction between living tissues and implant base material due to various bioinert coatings having high hardness value, resistance to mechanical wear and corrosion, and good adhesion to the substrate

2. Experimental setup

NbC and NbCN coatings were synthesized by vacuum-arc deposition on AISI 430 SS substrates of 25 × 25 × 3 mm size in "Bulat" type device. Before deposition, the substrates were cleaned in an ultrasonic bath with alcohol for 10 min. Chemically pure niobium (99.99 %) was used as a cathode material. First, the pulsed negative biasing of 1000 V with a frequency of 50 kHz was applied to the sample holder for substrate cleaning and degreasing. Next, a thin Nb buffer layer of 20 nm thickness was deposited before the carbide and carbonitride coatings to improve coatings adhesion. For NbCN coatings the N_2 and C_4H_{10} gas mixture was used. The nitrogen pressure in the deposition process was about 4.5×10^{-3} Torr and the CH pressure was 6.5×10^{-3} Torr. The deposition rate was ~ 35 μm/h. Deposition time ~ 13 min.

3. Results and discussion

Carbonitride film shows two phase state with diffraction peaks from cubic phase of NbC and hexagonal phase of $NbN_{0.95}$ in accordance with ASTM card 23-1363 (Fig.1). Niobium nitrides and carbides generate compounds with ionic and covalent bonds. The ionic character

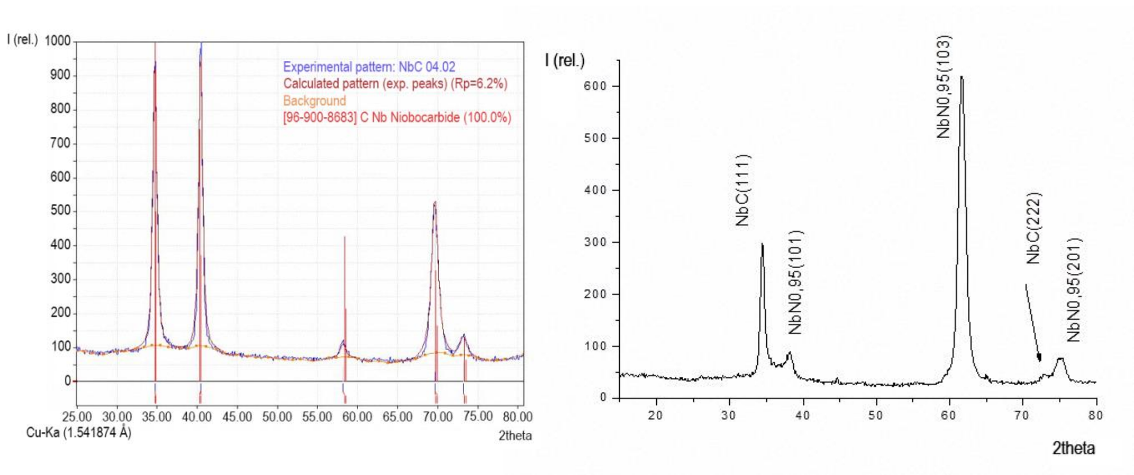

Fig. 1. XRD diffraction patterns taken from NbC (a) and NbCN (b) coatings

for NbN is of 40.04 % and NbC presents an ionic character of 18.3 %. Introducing nitrogen or carbon atoms into the niobium crystalline structure induces structural changes from a body centered cubic (BCC) with a cell parameter of 3.3280 Å to a NaCl like structure with a cell parameter of 4.4790 Å where Nb^+ cations occupy interstitial sites between atomic sites of the FCC carbon cell. The surface morphology and chemical composition of NbC and NbCN coatings were examined by using scanning electron microscope JEOL JSM-6390LV, equipped with EDX (Fig. 2.). The surfaces of both coatings are similar with faceted structure and very smooth having a small number of macrodefects identified as drops from the cathode material. The size of macroparticles does not exceed 2 μm. In accordance with energy-dispersive X-ray analysis the integral chemical composition of NbC coating was: Nb – 66.86 at. %, O – 4.61 at%, C – 28.53 at.%. The chemical composition of NbCN coating was: Nb – 25.68 at. %, C- 36.35 at.%, N- 34.58 at. %, O - 3.38 at. %.

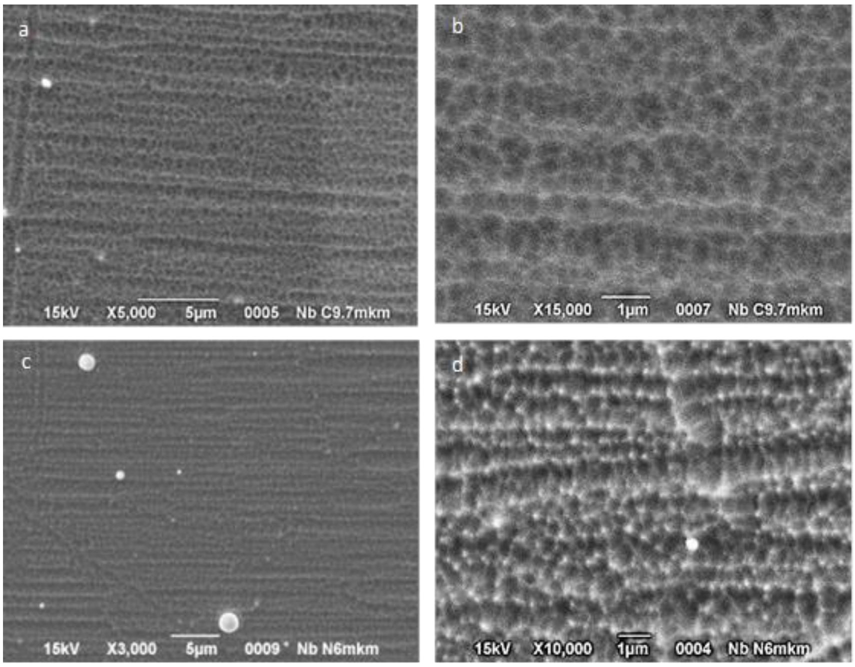

Fig.2. SEM images taken from NbC (a, b) and NbCN (c, d) coatings

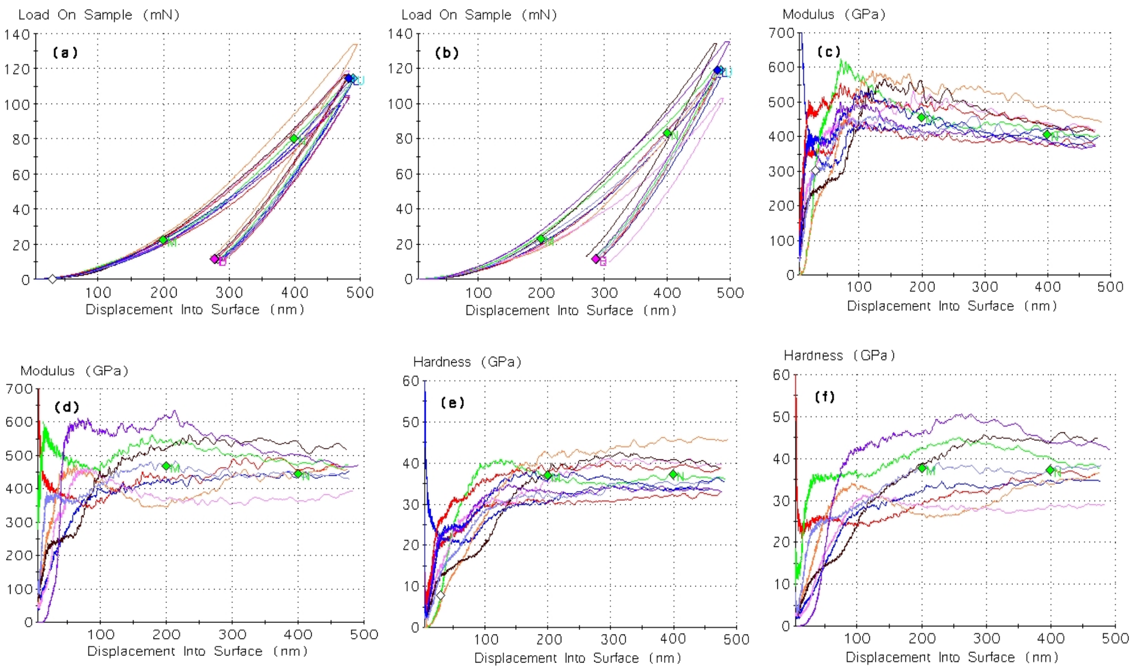

Fig.3. Nanoidentation diagrams for the NbC and NbCN coating; (a-f) load-unload diagrams, nanohardness, and elastic modulus

The nanoidentation diagrams for NbC and NbCN coatings are presented in Fig. 3.The results of H and E values, G, σT, and H^3/E^{*2} were obtained. These hardness values of the niobium-based coatings are higher than the hardness of stainless steel substrates, which was also measured in mirror-polished samples (~ 4 GPa), suggesting that there is essential improvement of the surface mechanical properties by the deposition of any of the coatings. Such high hardness is achieved due to formation of a nanocomposite structure consisting of two or more phases coexisting in a very small volume, crystals having dimensions of 2–20 nm.

Conclusions

Niobium-based coatings were deposited by using an ion-plasma vacuum-arc deposition technique with pulsed biasing mode on stainless steel (SS) substrates to evaluate them as possible surfaces that might extend the lifetime of SS dental implants. The proposed technology allowed minimizing the amount of micro-arc formations. Additional magnetic coil for plasma flow focusing was used, allowing one to enhance deposition rate up to 35 μm/h. The XRD data from NbC coating revealed the existence of a niobium carbide phase with NaCl-type lattice with fine-crystalline grains ranging from 14 to 16 nm. For the NbCN coating, the two-phase state with c-NbC and hexagonal $NbN_{0.95}$ phases was monitored. The average grain size for c-NbC phase comprised 16–17 nm; whereas, for $NbN_{0.95}$ the average grain size was only 1–2 nm, confirming formation of a nano-crystalline structure. It was revealed that nanohardness for NbC coating varied from 30–43 GPa; whereas, for NbCN the data spread comprised 30–48 GPa.

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