Development of Niobium Based Coatings Prepared by Ion-Plasma Vacuum-Arc Deposition

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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 the pulsed biasing mode with repetition frequency 50 kHz, allowing decreasing the micro-arcs formation. An additional magnetic coil for plasma flow focusing was used, allowing one to enhance deposition rate up to 35 $\mu\text{m/h}$. The phase composition of the obtained coatings was analyzed via X-ray diffraction. The surface morphology was monitored by scanning electron microscopy; whereas, chemical composition was examined by using energy dispersive X-ray analysis. X-ray fluorescent analysis was used to evaluate the thickness of the coatings. The reflectance $R(\lambda)$ of the obtained coatings in the wavelength 300–625 nm at normal incidence was measured. The XRD data from NbC coating revealed the existence of the niobium carbide phase with a 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 $\text{NbN}_{0.95}$ phases was monitored. The average grain size for c-NbC phase comprised 16–17 nm; whereas, for $\text{NbN}_{0.95}$ the average grain size was only 1–2 nm, confirming formation of a nanocrystalline structure. Surface nanomechanical behavior under nanoindentation of NbC and NbCN was studied. It was revealed that nanohardness for a NbC coating was varied from 30 to 43 GPa; whereas, for NbCN the data spread comprised 30–48 GPa. It was established that the surface of the grown coatings was very smooth with an extremely low amount of macroparticles.

KEY WORDS: coating, structure, nanohardness, niobium carbonitride, niobium carbide, ion-plasma vacuum-arc deposition, pulsed biasing mode

I. INTRODUCTION

Transition metals, such as tantalum and niobium, are excellent candidates as biocompatible coatings for various medical applications including dental implants.^{1,2} Nb has a lower melting point, lower density, and greater availability and therefore has lower cost in comparison to 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, the nuclear industry, and more.

Niobium has largely been used in Ti-6Al-4V titanium alloys to replace strong cytotoxic vanadium and Al associated with Alzheimer's disease.^{3,4} Nb has good corrosion resistance, osteogenesis and biocompatibility; in fact, it is one of the elements that does not produce an adverse reaction with surrounding tissues.^{5,6} Matsuno et al.⁷ implanted Ti, Hf, Nb, Ta, and Re in rats to investigate their osteoconductivity and proved that the amount of new bone formed around the Nb implant after four weeks is higher than that formed around the other samples, indicating better osseointegration of the Nb implant. In terms of mechanical properties, Nb and its alloys have been used for their good mechanical resistance, high melting point and high hardness, and even as reinforcement particles on composite materials with a metal matrix.⁸

The niobium coatings, with the addition of nitrogen and carbon, have a superior performance related to the surface wear reduction and lower corrosion rate compared to uncoated 316L stainless steel substrate and substrate coated with Nb. This behavior could be explained by the presence of NbC and NbN phases identified by means of X-ray diffraction (XRD) and the modification it induces in the Nb cubic structure.⁹ Such a combination of physical properties indicates a complex chemical bonding between the metallic element and carbon. The crystalline structure is typically of the NaCl-type or hexagonal, as is observed for the carbides of the early transition metals.¹⁰ It was reported by Xu¹¹ that the NbC films obtained with nonreactive and reactive magnetron sputtering on silicon (100), glass, and AISI 316LVM steel has the highest potential for dental implant surface modification in comparison to Nb, NbO, and NbN films. The nanohardness values were rather low and comprised Nb = 6.6 GPa, NbC = 12.0 GPa, NbN = 16.0 GPa, and NbO = 7.8 GPa.

Techniques such as chemical vapor deposition and physical vapor deposition allow applying Nb, NbC, NbN, and Nb₂O₅ of a huge variety of materials with different composition and microstructure. Mostly, Nb based coatings have been applied by using direct current (DC) or radio frequency (RF) magnetron sputtering.¹² However, 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 a 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.

A. Materials and Methods

NbC and NbCN coatings were synthesized by vacuum-arc deposition on AISI 430 SS substrates of 25 × 25 × 3 mm size in a Bulat-type device, described elsewhere.¹³ 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 10 × 10² 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 $\sim 35 \mu\text{m/h}$ and deposition time was ~ 13 min.

The surface topography of NbC and NbCN were studied using a JEOL JSM-6390LV scanning electron microscope (SEM) with an accelerating voltage of 20 KV, and the chemical composition was examined using energy-dispersive X-ray analysis (EDX). An energy-dispersive spectrometer SPRUT-K (AO Ukrrentgen, Ukraine) was used for X-ray fluorescent analysis and equipped with a Sc (Li) X-100 detector (Amptek, Bedford, MA) in the arrangement with Si and KCl secondary target. Film thickness was determined by X-ray fluorescent analysis examinations and comprised $6 \mu\text{m}$ for NbCN and $9.7 \mu\text{m}$ for NbC coatings. X-ray diffraction (XRD) analysis were performed using a DRON-3M device, under Cu-K α radiation, monochromated by (002) HOPG in a diffracted beam. The XRD line scans were performed in θ -2 θ scanning mode, where the incident angle θ and diffracted angle 2θ were scanned simultaneously.

The nanohardness was measured by a Nanoindenter G200 (Agilent Technologies Inc, Santa Clara, CA, USA). The loading and unloading rates of the nanoindentation were 10 mN. Samples were tested to a depth of 500 nm. Eight prints were made for each sample, and the distance between prints was $15 \mu\text{m}$. Reflectance (R) at normal incidence in the wavelength range of 300–625 nm was measured by using a microscope spectrophotometer MCFU-K (LOMO).

II. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the XRD spectra of both NbC and NbCN coatings. The NbC spectrum in Fig. 1(a) shows peaks with crystallographic planes (111), (002), (022), and (113) corresponding to the phase NbC of cubic modification ($a = 4.46910 \text{ \AA}$) in

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

accordance with the ICDD 96-900-8683 reference pattern. No additional phases were detected. The carbonitride film shows a 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.

Niobium nitrides and carbides generate compounds with ionic and covalent bonds. The ionic character for NbN is of 40.04%, and NbC presents an ionic character of 18.3%.⁸ 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 a face-centered cubic (FCC) carbon cell. The crystallite size of the coatings was calculated from the full-width-at-half-maximum (FWHM) intensity (β) of the X-ray diffraction angle (θ) of the diffraction peak and the wavelength (λ) of the copper X-ray radiation using the Debye–Scherrer relation,¹⁴ assuming that no strains were developed in the coatings

$$D = \frac{K\lambda}{\beta} \cos \theta \quad (1)$$

where K is an X-ray radiation-dependent constant ($K = 0.9$ for Cu-K α) and θ is the diffraction angle. The crystallite size of the niobium carbide film deduced was 14–16 nm. For the two-phase NbCN coating, the grain size of NbC phase was 16–17 nm and for NbN_{0.95} comprised 1–2 nm.

The surface morphology and chemical composition of NbC and NbCN coatings were examined by using a scanning electron microscope (JEOL JSM-6390LV), equipped with EDX (Figs. 2(a)–2(d)). The surfaces of both coatings are similar with a faceted structure and very smooth, having a small number of macrodefects identified as drops from the cathode material. The size of macroparticles < 2 μ m.

In accordance with energy-dispersive X-ray analysis (Figs. 3(a) and 3(b)), the integral chemical composition of the NbC coating was Nb – 66.86 at.%, O – 4.61 at.%, and C – 28.53 at.%. The chemical composition of NbCN coating was Nb – 25.68 at.%, C – 36.35 at.%, N – 34.58 at.%, and O – 3.38 at.%. The presence of a small quantity of oxygen is due to residual gas incorporated in the chamber walls and contamination during sample handling in an open atmosphere before the composition analysis.

The microhardness of the coating strongly depends on structural parameters such as crystallographic orientation, microstress, and crystallite size. One of the main characteristics of the material is the ratio of its hardness to the elastic modulus H/E , called plasticity index. The ratio H^3/E^{*2} , where $E^* = E/(1 - \mu^2)$ – the effective elastic modulus; μ – Poisson's ratio, is also a qualitative comparative characteristic of the plastic deformation resistance. To increase the plastic deformation resistance, it is required to strive for the lowest possible elastic modulus at high hardness, which, in particular, takes place at grain sizes of < 10 nm.

The effective elastic modulus E^* , the shear modulus G , yield stress point σ_T , and coefficient of resistance to plastic deformation H^3/E^{*2} were determined using model equations. The shear modulus and yield stress are defined as follows: $G = E/2 \times (1 + \mu)$; $\sigma_T = H\mu/3$.

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

FIG. 3: EDX spectra of (a) NbC and (b) NbCN coatings

The nanoindentation diagrams for NbC and NbCN coatings are presented in Fig. 4. The results of H and E values, G , σ_T , and H^3/E^2 are summarized in Table 1. 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

FIG. 4: Nanindentation diagrams for the NbC and NbCN coating: (a-b) load-unload diagrams, (c-d) elastic modulus and (e-f) nanohardness, respectively

TABLE 1: Mechanical characteristics of niobium-based coatings

Sample	E GPa	H GPa	H/E	H^3/E^2	E^*	H^3/E^{*2}	G, GPa	σ_p , GPa
Average data from eight prints								
NbCN	465.588	36.812	0.079	0.233	496.627	0.205	290.992	12.271
NbC	428.073	35.901	0.084	0.253	456.611	0.222	267.55	11.97
AISI 430 SS	201.151	4.092	0.020	0.001	230.231	0.05	121	9.66

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. In the case of nanocrystalline materials, the number of atoms in the crystalline grain is comparable to or even less than the number of atoms within the grain. In such conditions, the formation of dislocations is inhibited by the grain boundary, and mechanical deformation occurs by the mechanism of sliding beyond the grain rather than by the dislocation of motion, which is a deformation mechanism in ordinary materials. This leads to a significant increase in the hardness of nanocrystalline materials and to the development of superhard materials.

Reflectance of the niobium-based coatings was measured in the range from 300 to 625 nm and compared to mirror-polished AISI 430 stainless steel substrate. The data obtained are presented in Table 2. The results showed in a decrease in reflectance as compared to the case of initial stainless steel surface. Figure 5 shows a graph representation

TABLE 2: Reflectance characteristics of niobium-based coatings in comparison to initial AISI 430 surface

	Wavelength λ , nm													
	300	325	350	375	400	425	450	475	500	525	550	575	600	625
Samples	<i>R</i> , %													
AISI 430	27.2	32.4	36.3	37.7	41.3	42.3	44.2	45.4	45.8	46.6	48.6	47.3	49.9	50.8
NbCN	7.8	8.3	9.1	9.8	10.6	12.0	12.6	14.1	15.1	16.2	17.0	18.1	18.7	18.5
NbC	9.5	10.1	10.6	11.4	12.0	12.7	14.1	15.9	18.7	20.9	23.6	26.0	28.5	29.4

FIG. 5: Wavelength dependences of the initial reflectance (AISI 430 SS) and the reflectance of NbCN and NbC coatings

of wavelength dependences of the initial reflectance (AISI 430 SS) and the reflectance of NbCN and NbC coatings.

III. 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 $\mu\text{m}/\text{h}$. 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 $\text{NbN}_{0.95}$ phases was monitored. The average grain size for c-NbC phase comprised 16–17 nm; whereas, for $\text{NbN}_{0.95}$ 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. Reflectance of the niobium-based coatings was measured in the range of 300–625 nm and compared to mirror-polished AISI 430 stainless steel substrate. The proposed technology would be prospective for applying niobium coatings on dental implants made of stainless steel or Ti6Al4V alloy.

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