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Ion beam analysis, corrosion resistance and nanomechanical properties of TiAlCN/CN_x multilayer grown by reactive magnetron sputtering

B. Alemón¹, M. Flores¹, C. Canto², E. Andrade², O.G. de Lucio², M.F.Rocha³, E. Broitman⁴.

1. Departamento de Ingeniería de Proyectos, CUCEI, Universidad de Guadalajara, J. Guadalupe Zuno 48, Los Belenes, Zapopan Jal., 45101, México

2. Instituto de Física, UNAM, Avenida de la Investigación S/N, Coyoacán, México D. F., 04510, México.

3. ESIME-Z, Instituto Politécnico Nacional, ALM Zacatenco, 07738 México D. F., México

4. Thin Films Physics Division, IFM, Linköping University, Sweden, SE-58183 Linköping.

Abstract:

A novel TiAlCN/CN_x multilayer coating, consisting of nine TiAlCN/CN_x periods with a top layer 0.5 μm of CN_x, was designed to enhance the corrosion resistance of CoCrMo biomedical alloy. The multilayers were deposited by dc and RF reactive magnetron sputtering from Ti_{0.5}Al_{0.5} and C targets respectively in a N₂/Ar plasma. The corrosion resistance and mechanical properties of the multilayer coatings were analyzed and compared to CoCrMo bulk alloy. Ion beam analysis (IBA) and X-ray diffraction tests were used to measure the element composition profiles and crystalline structure of the films. Corrosion resistance was evaluated by means of potentiodynamic polarization measurements using simulated body fluid (SBF) at typical body temperature and the nanomechanical properties of the multilayer evaluated by nanoindentation tests were analyzed and compared to CoCrMo bulk alloy. It was found that the multilayer hardness and the elastic recovery are higher than the substrate of CoCrMo. Furthermore the coated substrate shows a better general corrosion resistance than that of the CoCrMo alloy alone with no observation of pitting corrosion.

Key words: Ion beam analysis; corrosion; TiAlCN/CN_x multilayer coating; nanoindentation.

1. Introduction

Nowadays, CoCrMo alloys are used in prosthetics manufacturing for both hip and knee implants due to their biocompatibility and also due to superior mechanical properties and high wear resistance than other biocompatible materials [1]. However disadvantages during real use have been reported, including lower resistance to corrosion and decreased biocompatibility due to the release of metal ions in the body compared to Ti₆Al₄V [1-4]. One way to improve the properties of CoCrMo alloys without losing their mechanical properties is to apply coatings by physical vapor deposition (PVD) methods [5-7].

It has been shown that nitride coatings, such as titanium nitride (TiN) [8] and titanium nitride-aluminum nitride TiN/AlN [9], and tetrahedral amorphous carbon films [10], deposited over CoCrMo alloy substrates are biocompatible and they have good tribological properties that improve the prosthesis material both in performance as well as length of useful life [11, 12]. Additionally, Broitman et al. have found that CN_x films layered on orthopedic substrates such as ZrO₂ present a low coefficient of friction (COF) below 0.18 when they were evaluated against ultra-high molecular weight polyethylene (UHMWPE) in the presence of human serum lubricants. Their research has further demonstrated that the CN_x films possess the potential to generate low wear conditions for these polymer [13]. Other investigations have shown that multilayers improve the corrosion and wear resistance of the substrate [14, 15]. However the use of multilayer coatings for biomedical applications has attained relatively low attention.

This work reports studies of a novel TiAlCN/CN_x multilayer deposited on CoCrMo biomedical alloy by reactive magnetron sputtering with the purpose of enhancing corrosion resistance of the substrate.

The quality of the coatings depends on their elemental composition and it is related to the PVD deposition parameters. For an optimization of the deposition parameters it is necessary to know the absolute content of Ti, Al, N and C. The analysis of the layers with N and C with RBS suffers in many cases from the difficulty to quantify these elements because of the relatively small sensitivity compare to heavy elements. A combination of Rutherford backscattering (RBS) with Nuclear Reaction Analysis (NRA) techniques allowed a precise determination of the Ti, Al, N and C elements profile without ambiguity. The NRA was performed with a 1300 keV deuterium beam and the RBS with a 2000 keV ⁴He beam. The hardness and reduced

Young's modulus were investigated by nanoindentation technique and the corrosion resistance in simulated body fluid (SBF) was studied by potentiodynamic polarizations tests.

2. Experimental details

Discs of low carbon CoCrMo alloys (ASTM F 1537, C(0.04%), Mo(0.81%), Cr(27.58%), Co(64.99%) of 31.75mm in diameter and 6mm thick were ground flat with sandpaper of 240, 400, 600, 1200 grades and subsequently polished with diamond paste until a roughness of R_a of $0.03\ \mu\text{m}$ (measured with a Dektak 150 profilometer) was achieved. Before the deposition, the substrates were ultrasonic cleaned for fifteen minutes in acetone and then in isopropyl alcohol and dried with clean air. The multilayers were deposited by DC and RF reactive magnetron sputtering from TiAl and C targets respectively in N_2/Ar plasma. The substrate rotates in the process at a distance of 60 mm from the targets. A pure titanium target (99%), a high purity (99.99%) graphite target and a high purity (99.95%) $\text{Ti}_{0.5}\text{Al}_{0.5}$ target were used during the experiments. Fig. 1 shows a schematic diagram of the arrangement of the targets in the vacuum chamber. The multilayer nominal composition consists of 9 periods of TiAlCN (180nm thick) alternating with CN_x (60nm thick) layers. The first deposit on the substrate was a titanium layer (100nm thick) to promote adhesion of the multilayers deposit. Also a CN_x layer on the top of the coatings (480nm thick) was deposited. Fig. 2 shows a schematic diagram of the multilayer coating. For statistical purposes, five similar coatings were prepared for these studies.

Fig.1. PVD targets arrangement for the sputtering process deposition of the TiAlCN/CN multilayer coating

Fig.2. Schematic representation of the experimental design of the multilayer film composition and film thickness. The total coating thickness ranges from 2.7 to 3 μm .

The initial vacuum pressure of the deposition chamber was $\sim 3.9 \times 10^{-4}$ Pa (3×10^{-6} Torr). The substrates were preheated at 125°C for 30 min and sputter cleaned using radio frequency (RF) applied to the substrates at argon pressure of ~ 0.26 Pa (2m Torr) with a power of 40 watts for 20 minutes.

Multilayer TiAlCN/CN_x was grown at a temperature $\sim 125^\circ\text{C}$. The first titanium layer on the substrate was deposited by sputtering the Ti target in an Ar discharge at a pressure of .26 Pa (2mTorr) and DC constant current of 0.6 A. The TiAlCN layers were obtained by codeposition of TiAl using a DC source with a constant current of 0.6 A and graphite with the AC power source (RF) at a power density of 10 W/cm^2 . The CN interlayer and top layer was obtained with RF power of 200 W. During the deposition of the multilayers a bias voltage of -40 V was applied to the substrate. The flow rate of Ar/N₂ was changed during the deposition process and it was 60/40 for TiAlCN and 43/57 for CN. Each layer was deposited without turning off the plasma in order to obtain a gradual change between the layers.

A vertical single ended 5.5 MV Van de Graff accelerator was used to apply a combination of the RBS technique with a 2000 keV ^4He beam and the NRA technique with a 1300 keV deuterium beam. Each sample was bombarded at the same beam spot at normal beam incidence. A surface barrier detector (SBD), located 150° degree with standard electronic, recorded the particle energy spectra.

For the NRA experiments the deuterium beam current was relative high (about 100 na) and the SBD had in front a 15 microns kapton film to absorb the elastically backscattered deuterium from the target nuclei in order to measure only the high energy NR particles from the (d, p) and (d, α) nuclear reactions produced by the

bombardment on C and N nuclei. The NR cross sections of these nuclei are two or three orders of magnitude smaller compare to the RBS cross sections, producing a low particle counting rate. A big solid angle was used with this SBD in order to measure more efficiently the NR particles and to obtain a NRA spectrum in a short time with a good statistics.

The crystal structure of the low CoCrMo alloy substrate and multilayer coating was analyzed using Cu K α ($\lambda=0.15406$) in Siemens D500 X-Ray diffractometer. A conventional $\theta/2\theta$ Bragg–Brentano symmetric geometry was used, from 20° to 100°, with a step size of 0.03° and a time step of 1 s.

The mechanical properties of TiAlCN/CN_x and the substrate were evaluated by nanoindentation experiments in a TI 950 triboindenterTM (Hysitron). Hardness (H) and reduced Young's modulus (E_r) were measured using a Berkovich diamond indenter. The values were calculated according to the method by Oliver and Pharr [16]. In order to avoid the combined effect of the coating and the substrate, penetration displacement was slightly less than 10% of the total coating thickness. In all depth-sensing tests a total of 10 indents were averaged to determine the mean H, E_r and their standard deviation. The displacements were continuously recorded during the indentations. The penetration displacement of the indenter at maximum load (h_{max}) and the final displacement h_f recorded in the unloading curve were used to determine the percentage of elastic recovery (%R) [17].

$$\%R = \left(\frac{h_{max} - h_f}{h_{max}} \right) (100) \quad (1)$$

The electrochemical study was carried out using a potentiostat Gamry reference 600. The SBF prepared according the method of Kokubo et al. [18] was used as electrolyte in the measurements. The test was performed using a three electrode cell. A saturated calomel electrode (SCE) was used as the reference electrode, a flat platinum wire as counter electrode and the sample as working electrode. The temperature of the electrolyte is controlled by a recirculation of water at 36.5°C $\pm$ 1.5°C. The sample was immersed in 50ml SBF solution with $\sim 1 \text{ cm}^2$ exposed area.

The corrosion resistance of the multilayer was evaluated using potential-current curves obtained by potentiodynamic polarization. All the potentials reported

here are referred to the SCE. The corrosion current density i_{corr} was estimated by linear fit and Tafel extrapolation to the anodic part of the polarization curve.

3. Results and discussion

3.1 Ion beam results

Fig. 3 shows a RBS spectrum from a 2000 keV ^4He bombardment of one of the multilayer TiAlCN/CN_x coatings while Fig. 4 shows a portion of the NRA spectrum obtained with a deuteron beam with energy of 1300 keV from the irradiation on the same spot in the sample. The solid line represents the SIMNRA [19] simulation of the spectra used to obtain the atomic profiles shown in Fig. 5 of the four elements in the coating. RBS cross sections for the Ti and Al and non RBS cross sections for elastic backscattering N and C were used to simulate the spectrum. The difficulty to quantify N and C from the RBS spectrum due to its small sensitivity compare to heavy elements was resolved by the simultaneous simulation of the NRA and RBS spectra. Some of the NR peaks identified in the NRA spectrum used for the simulation were: $^{14}\text{N}(d, \alpha_1)^{12}\text{C}$ [20], $^{14}\text{N}(d, p_3)^{15}\text{N}$ [21], $^{14}\text{N}(d, \alpha_0)^{12}\text{C}$ [22], and $^{12}\text{C}(d, p_0)^{13}\text{C}$ [23]. The numbers inside the parenthesis are the reference of the NR cross sections from the IBANDL (ion beam analysis data library) data base.

Fig.3. RBS spectrum from a 2000 keV ^4He bombardment of one of the multilayer TiAlCN/CN_x coatings on CoCrMo substrate. The multilayer structure of the coating can be observed due to the ^4He good energy depth resolution. The solid line represents the SIMNRA simulation of the spectrum. The Ti, Al, N and C partial contributions in the simulation are also plotted.

Fig.4. Segment of the NRA spectrum from the 1300 keV deuterium bombardment of the coating in the same beam spot of the RBS. The solid line represents the SIMNRA simulation of the spectrum.

Fig.5. The Ti, Al, N and C atomic (%) profiles of the TiAlNC/CN_x obtained from the SIMNRA simulation of the RBS and NRA spectrum from Fig.4 and Fig. 5

In Fig. 5, the elemental profile for C, N, Al and Ti are shown for the whole film. Ti and Al are absent in some part of the depth profile and this is a consequence of the multilayer design. It is also shown in Fig 5, that there are clear gaps between the layers with aluminum and those without it, which demonstrate no diffusion of the heavy elements Ti and Al in CN layers.

3.2 XRD results

Fig. 6 shows the diffractogram of a TiAlCN/CN multilayer coating deposited onto CoCrMo compared to a CoCrMo diffraction pattern. Both XRD plots matches together but the intensity of the coated CoCrMo substrate peaks are attenuated by ~ 60-70% due to the presence of the multilayer coating. The XRD did not reveal the presence of extra peaks indicating that the multilayer has an amorphous structure, as we expected because of the low substrate temperature used during the deposition process [17].

Fig.6. XRD diffraction patterns from the CoCrMo coated with the TiAlCN/CNx multilayer and CoCrMo substrate

3.3 Nanoindentation results

Fig. 7 compares the load displacement curves from nanoindentation measurements for the TiAlCN/CN_x multilayer coating and the uncoated CoCrMo substrate. Table 1 shows hardness (H) and reduced Young's modulus (E_r) calculated according Oliver-Pharr approach [16]. The multilayer is slightly harder than the substrate but its E_r is 50% lower than substrate. The percentage of elastic recovery (%R) of the multilayer resulted 68%, 2.6 times higher than the %R of the substrate due to the thick top layer of CN_x on the multilayer coating, as it has previously shown by Broitman, *et al.* [17]. We conclude that our design of the multilayers deposited onto the CoCrMo alloys improves the mechanical properties of the substrates and will probably increase their life time [24].

Fig.7. Nanoindentation load displacement curves from TiAlCN/CN_x multilayer coating in comparison with CoCrMo curves

Table1. Values of Hardness, E_r and % elastic recovery of CoCrMo substrate uncoated and coated with TiAlCN/CN_x multilayer

	Hardness (Gpa)	Reduced Young's Modulus(Gpa)	Elastic Recovery %
CoCrMo Substrate in SBF	8.69 +/-0.3	186.9 +/-4.6	26.2 +/-4.6
TiAlCN/CN _x	10.8 +/-0.9	86.3 +/-3.2	68.2 +/-2.2

3.4 Corrosion resistance results

In comparison to the uncoated substrate, the potentiodynamic polarization tests results indicated a better behavior for corrosion in SBF of the substrate coated with TiAlCN/CN_x multilayer. Fig. 8 shows that the pitting corrosion potential of the CoCrMo starts at ~0.44 V. On the other hand, at the same potential, there is no change in the anodic part of the potentiodynamic curve of the TiAlCN/CN_x indicating that there is not pitting corrosion for the multilayer coated substrate in the studied interval. In Table 2, the value of E_{corr} of the uncoated CoCrMo alloy is more negative than the TiAlCN/CN_x, which indicates that the coated sample has a lower tendency to be corroded. The I_{corr} value of the uncoated CoCrMo obtained by Tafel extrapolation is three times higher than the multilayer coated CoCrMo. We can then conclude that the multilayer coating provides a higher corrosion resistance to general and localized corrosion.

Fig.8. Potentiodynamic polarization curves for the multilayer coated and uncoated surfaces of CoCrMo.

Table 2. Values of E_{corr} , I_{corr} and pitting corrosion of CoCrMo substrate uncoated and coated with TiAlCN/CN_x multilayer

	E_{corr} (Volts)	I_{corr} (A/cm ²)	$E_{\text{pitting corrosion}}$
CoCrMo Substrate in SBF	-0.28	7.24×10^{-8}	0.44
TiAlCN/CN _x	-0.12	2.14×10^{-8}	None in the potential interval

4. Conclusions

A novel multilayer film of TiAlCN/CN was designed and deposited on a CoCrMo substrate by reactive magnetron sputtering technique.

A couple of ion beam analysis techniques (RBS and NRA) were used to analyze the elemental profile of the film, and the results were applied to correlate the deposition parameters with the composition and thickness of every layer of the multilayer coating. The combination of both techniques and the simultaneous simulation of the RBS and NRA spectra allow us to determine the Ti, Al, N and C elements profile with reduced ambiguity.

XRD analysis results have confirmed that the multilayer coatings are amorphous.

Nanoindentation experiments strongly suggest that the TiAlCN/CN_x multilayer coating has improved the mechanical properties of the uncoated substrate, with higher hardness and elastic recovery.

Potentiodynamic polarization tests indicated a better behavior for corrosion of the multilayer coating in SBF.

It can be concluded that the CoCrMo substrate coated with the designed TiAlCN/CN_x multilayer provides to the substrates improved mechanical properties and increased protection against pitting and general corrosion.

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