Nanomechanical and elastic properties of TiN coated dental materials determined by atomic force microscopy (AFM)

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In this research, nanolayered TiN layers were deposited on dental materials (titanium alloy, Co-Cr alloy, Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) and stainless steel (AISI 316) raw materials) by RF magnetron sputtering. Microstructure, surface topography, nanomechancial properties and elastic properties of TiN coated dental materials were analyzed using by atomic force microscopy (AFM). Stoichiometric ratio of N/Ti is ½. Penetration depth is arranged 5 nm, 10 nm, 15 nm and 250-400 nm. Nanomechanical and Young modulus were determined by depth sensing indentation test. Furthermore, nanohardness value of the stainless steel samples were increased to level of Y-TZP samples by TiN coatings.

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1. Introduction

Titanium nitride (TiN) is a member of the refractory transition metal nitrides family, which exhibits properties characteristic of both covalent and metallic compounds [1]. TiN has many advantages such as including intrinsic biocompatibility, sufficient corrosion resistance, reduction of bacteria, and its suitability for use in patients who have a metal allergy to vanadium, nickel and cobalt [2-4]. TiN is also a suitable material for the hard coating of dental materials such as implants and dental surgical instruments in order to improve their surface properties [5].

In particular, the TiN coating that provides a diffusion barrier and biocompatible surface has been applied using a metal sputtering technique in order fabricate biocompatible prostheses [5,6]. TiN coated dental samples show higher physico-mechanical properties [1]. Moreover, TiN coating could affect the topographic and the mechanical features of other dental materials (Co-Cr, Y-TZP, Stainless-Steel). These surfaces have not been extensively investigated.

There are many different type of dental materials. In this paper, dental materials were coated with very thin layers of TiN. Hardness property of the dental materials is one of the major properties. Hardness can be defined as resistance to permanent surface indentation or penetration [7].

In this study, nanolayered TiN coatings were deposited onto the dental titanium alloys, Co-Cr alloys, Y-TZP ceramic and stainless steel (AISI 316). These coatings were realized by relatively high pressure reactive RF magnetron sputtering. The thicknesses were determined using an interferometer. XRD tool was used for microstructure and crystallographic data of coated layer. The surface topography and nanomechanical properties of the produced films were analyzed atomic force microscopy (AFM). AFM is a non-destructive modern imaging technique with nanometer and sub-nanometer resolution [8, 9].

2. Experimental

The RF sputtering system was used for the depositions of TiN. An RF power supply of 13.56 MHz was used. The sputtering target was a commercial product bought from the firm J. Kurt Lesker. Its diameter was 2 inches. The distance between the sputter target and the dental materials was adjust to 50 mm. The coatings were deposited in a high argon–nitrogen gas mixture (1:1) atmosphere. The working pressure was adjusted to a relatively high level of 200 mTorr. The RF power was adjusted to 100 W. Whole samples were prepared for 60 min. Dental materials were prepared from titanium grade 5 (Ti-6Al-4V) alloy (Biotec srl, Povolaro di Dueville, Italy), Co-Cr (Magnum Lucens, Type 4) alloy (MESA, di Sala Giacomo & C. S.n.c. Travagliato, Italy), Y-TZP (3M ESPE Dental Products, St. Paul MN/USA) ceramic and stainless steel (AISI 316). High quality polishing and cleaning process were applied before the coating process. Mechanical polishing was performed to reduce the surface roughness. The samples were cleaned in 96 % ethanol and distilled water. The dental samples were coated with a thickness of 50 nm TiN. Nanoindentation is commonly used for the determination of mechanical properties of nano layered coated materials [10].

AFM is a powerful technique for observing the nanomechanical properties of the nanostructured materials on a very small scale at very high resolution. The hardness (H) and Young's modulus (E) of the coated surfaces are calculated from the load-unload curve from the nanoindentation experiment [9-16]. Oliver and Pharr's method is the best technique for determining the mechanical properties at the nanoscale for nanolayered and monolayer thin films. Additionally, this technique may determine the depth profile of the mechanical properties. This technique is also called the depth-sensing nanoindentation technique [9-16]. The elastic properties are determined using

$$E_r = \frac{\sqrt{\pi}}{2\beta} S \frac{1}{\sqrt{A}} = \frac{\sqrt{\pi}}{2\beta} \frac{dP_{max}}{dh} \frac{1}{\sqrt{A}} \tag{1}$$

where S is the slope of the unloading curve of the nanoindentation (dP_{max}/dh), and E_r is the reduced modulus, A is the projected area of the contact, β is a constant that depends on the geometry of the intender, P_{max} is the maximum applied load.

Young modulus, E can be obtained from equation 2.

$$\frac{1}{E_r} = \frac{1-v^2}{E} + \frac{1-{v_i}^2}{E_i} \tag{2}$$

where, E_i (1140 GPa) and v_i (0.07) are the Young's modulus and Poisson coefficient of the indenter used in the AFM, respectively. E and v are the Young's modulus and Poisson coefficient of the tested coated layer, respectively.

For the hardness calculations, the coated layer hardness is calculated using [13]

$$H = \frac{P_{max}}{A} = \frac{4\beta^2}{\pi} \frac{P_{max}}{S^2} E_r^2, \tag{3}$$

where P_{max} is the maximum loading, and A is the projected area of the indentation impression of the push up force used on the indenter in the AFM.

The projected area A for Berkovich indenter is obtained as;

$$A(h_c) = 24.5\, h_c^2 \tag{4}$$

$$h_c = h_{max} - \varepsilon \frac{P_{max}}{S} \tag{5}$$

where, h_c, h_{max}, S and P_{max} values are measured from classical load-unload graphs given in Fig. 1. The value of ε is equal to 0.75 for this calculation [9-16].

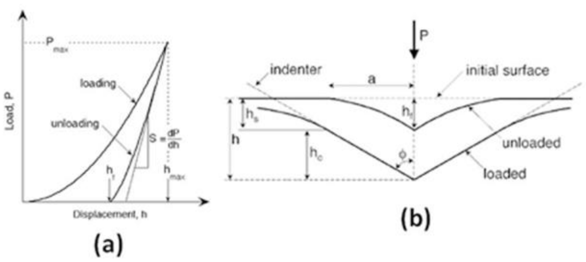

Fig. 1. Schematic illustration of (a) indentation load-displacement data, (b) the unloading process (These images were taken from references 12).

3. Results

Thicknesses of the coatings were measured as 50 nm using Filmetrics F20 interferometer. PANalytical Empyrean XRD was used for microstructure and crystallographic data of coated layer. Obtained XRD spectra are shown in Fig. 2. Crystal system of the coated layer is a Tetragonal phase. Chemical formula is N_1Ti_2 with 141/amd space group. A density of the coated layer is 4.83 g/cm^3.

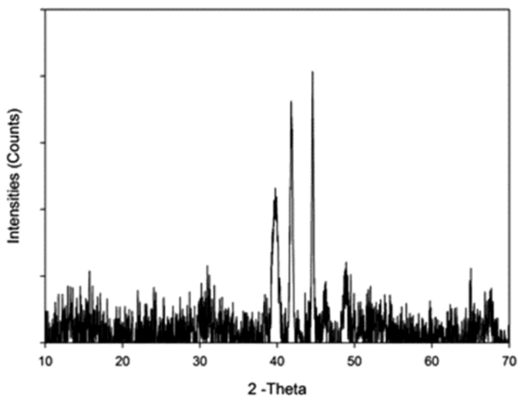

Fig. 2. XRD spectra of coated layer.

Surface imaging, roughness measurements and nanoindentations experiment were performed by Ambios Q-Scope atomic force microscopy. Roughness values were calculated from seven different measurements. Calculated average roughness values are approximately 17 nm, 30 nm, 104 nm, and 157 nm for TiN coated on Co-Cr, SS316, Ti-6Al-V, and Y-TZP, respectively. Obtained AFM images are shown in Fig. 3.

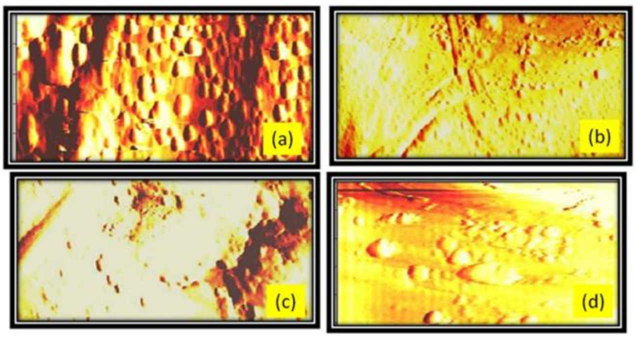

Fig. 3. Afm images of (a) Ti-6Al-V, (b) Co-Cr, (c) Y-TZP, and (d) SS316 samples.

Hardness values of the bulk Ti-6Al-V, Co-Cr, Y-TZP and SS316 are 3.8 GPa [16], 6,71 GPa [17], 13.6 GPa [18], and 3.8 GPa [19], respectively. Young modulus of the bulk Ti-6Al-V, Co-Cr [21], Y-TZP and SS316 are 110 GPa [20], 200-230 GPa, 215 GPa [22], and 193 GPa [23], respectively. These values were collected literatures.

Hardness and Young modulus of TiN coated specimens were determined by nanoindentations method. These values are plot in Fig. 4. Poisson rate of Ti-6Al-4V, Co-Cr, Y-TZP and SS316 are 0.342 [24], 0.300 [25], 0.250[26], 0.27-0.30 [27], respectively.

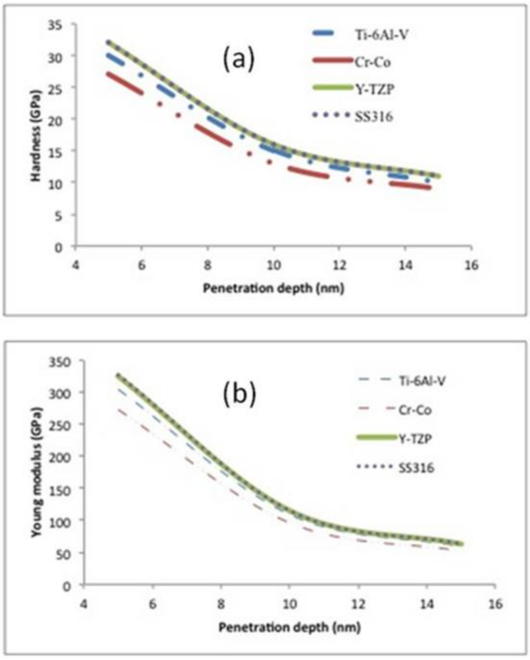

Fig. 4. (a) Hardness and (b) Young modulus graphs of Ti-6Al-V, Co-Cr, Y-TZP, and SS316 via penetration depths (nm).

4. Discussion

The hardness and Young modulus values of the coated TiN films at 5 nm, 10 nm and 15 nm nanoindentation depths were calculated. Nanoindentation experiments should be realized at approximately 10-20 % of the film thickness [9]. This paper focuses on to show differences of hardness values via penetration depth. Hence, we have not sticking to this rule. It should be noted that higher penetration depths measured hardness value includes the combined contribution of substrate and film. Calculated hardness values of coated Ti-6Al4V, SS316, Co-Cr and Y-TZP were calculated 3.3 GPa, 3.17 GPa, 2.56 GPa for and 2.33 GPa, respectively. These graphs are given in Fig. 5. It can be seen that both the hardness and Young modulus decrease with the increasing penetration depth. The hardness values increase with the decreasing nanoindentation depth. As can be seen in Fig. 4a and Fig. 5, the hardness values of the all-TiN coated samples are very close. It was found that TiN coated Y-TZP and SS316 materials are hard. Bulk Y-TZP hardness is 12.4 GPa. Other bulk material's hardness is approximately 4 GPa. These results showed that hardness values were dropped to very low value (approximately 3GPa) at high pressure values. This is the desired results because; material hardness should be close to hardness values of bone. Young modulus values of the cortical bone by nanoindentation technique were found 80 GPa [28].

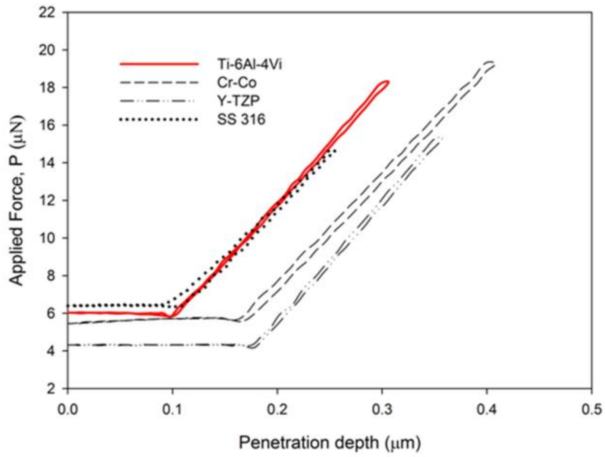

Fig. 5. Load-unload analyses data of TiN coated samples.

5. Conclusions

In this research, nanolayered TiN coated dental materials (titanium alloy, Co-Cr alloy, Yttria-stabilized tetragonal zirconia polycrystals and stainless steel 316) were prepared. These artificial dental specimens were coated by RF magnetron sputtering using pure TiN target. The nanomechanical results showed hardness and Young's modulus of the coated samples are very close to each others. Specially, stainless steel 316 hardness was increased to value of the Y-TZP hardness. Furthermore Hardness and Young modulus depth profile were determined. These values depth profile results are in good agreement with the literature.

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