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Mechanical Properties of Biocompatible (Ti,Al,V)N/ TIOx Coating for Titanium Implants

KEYWORDS: vacuum arc deposition, biocompatible coatings, (TiAlV)N/TiO_x, mechanical properties, grain size

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ABSTRACT *The analysis of nanomechanical properties of the materials for biological applications has become an increasingly useful tool on investigation of these materials. Although the biocompatibility of Ti has been confirmed, it is difficult to meet all the requirements, such as antibacterial ability, osseointegration and mechanical properties. Titanium alloys have a high friction coefficient while interacting with bone or tissue, which can cause wear debris pain and loosening of implants.This situation could be avoided using alloy surface modification by a durable, mechanically stable, wear resistant (TiAlV)N coating with a low friction coefficient as a base for an overlaying nanostructured TiOx.*

This article represents the research on the influence of the process of vacuum arc deposition of (TiAlV)N coatings and next vacuum oxidation on their mechanical properties and morphology. The microstructure, mechanical properties and applicability of the investigated (Ti,Al,V)N/TiO_x coatings for biocompatible titanium implants are discussed.

INTRODUCTION

The wear properties, Young's modulus, hardness characteristics, ductility, fretting fatigue life, etc., should be controlled so that their levels are suitable for structural biomaterials that replace hard tissue. All these characteristics may be collectively referred to mechanical biocompatibilities. The mechanical stability of orthodontic mini implants is mainly studied with regard to insertion torque or the force needed for pulling from the bone along the path of insertion [6]. Further fatigue strength of the biomaterial is of great importance for long-term success of the implant subjected to cyclic loading [14].

TiN has drawn an attention due to its mechanical properties, such as hardness, shear strength [4] and biological properties such as biocompatibility [21] and hemocompatibility [2]. Its usage is well documented in various biomedical applications [10, 13, 20]. However, TiN coating does not provide sufficient corrosion protection in some cases because of its porous structure. Comparing the surface of the TiN coated substrates with that of the TiO_2 coatings, biocompatibility is more pronounced in the latter case. Therefore, a promising option is to develop a new technology of nanocomposite biocompatible coatings on titanium alloys used in implants, based on the effect of the interaction of PVD (TiAlV)N coated implants with surface TiO_x obtained by vacuum oxidation. The way that PVD oxide and nitride layers interact inbetween and their bond strength are still insufficient investigated. So, investigation of surface hardness can contribute to the understanding of the biocompatibility of new materials by determining crucial surface information. The use of complementary evaluation methods of various mechanical properties can give us comprehensive information about the quality of applied coatings.

MATERIALS AND METHODS:

(TiAlV)N coatings with 4 μm thickness have been deposited on substrates of commercially pure Ti (cpTi) with size Ø20x6mm. The coatings have been deposited by reactive arcsputtering in a vacuum chamber under $2{,}5.10^{-3}$m bar pres sure, using TiAl6V4 target in nitrogen atmosphere at 150°C substrate temperature for time of 120 min., at 120 A arc current and -250V bias of substrates. Before deposition, the substrates first have been ultra soni call y was hed in ethanol,, acetone, is opropanol and distilled water for 5 min., and second have been additionally cleaned in the vacuum chamber by glow discharge in pure Ar atmosphere at pressure of $2{,}5.10^{-2}$mbar under substrate bias -400V for 60 min. To ensure the highadhesion and relaxation of the coating stresses,, a very thin under layer from the TiAl6V4 target at $2{,}5.10^{-3}$m bar in pure Aratmosphere for 5 min. have been previously deposited. Over the (TiAlV)N layera second TiOx film with 0,2-0,3 μm thickness was made by oxidizing, using glowdis charge under -400V biasin oxygen at mosphere at a pressure of $2{,}5.10^{-2}$ mbar for time of 90 min. The coated specimens were stored under dark ambient con ditions for four weeks, which allowed sufficient aging and standardize the surface energy.

Surface roughness parameters R_a and R_z of the substrates and coatings were measured by MITUTOYO Surftest SJ-201P contact stylus profiler. Coating thickness has been measured by CSEM-Calotest apparatus. The Martens hardness HU, plastic hardness H_{pl} and Young's modulus E of the (TiAlV)N/TiO_x coatings have been determined by a Vickers nanoindentation tester FISCHERSCOPE H100 using a load force of 50 mN. The coating adhesion and cohesion was evaluated by the "CSEM-REVETEST" scratch tester by progressive increasing load from 0 to 50 N. The texture and width of column of the as-deposited films was examined by XRD using URD-6 diffractometer and the (220) peak was typically selected for width of column measurements. The grain size d is calculated from the width of the diffraction peaks according to the equation [17]:

(1) where: λ – wavelength of FeKα radiation; θ – angle of

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diffraction peak position; β - full width of the half diffraction maximum.

RESULTS AND DISCUSSION

The values of coating hardness HU and H_{pl}, both calculated from the force-depth data corresponding to the nanoindentation test, performed at 500 and 50 mN peak load respectively are plotted in Table 1. For both situations, the H_{pl}/E and H_{pl}^3/E^2 ratios are also calculated and shown in Table 1. The values, represented in the table, show the increasing of the hardness after the coating deposition, which results in increase of the wear resistance.

TABLE 1. Experimental results of hardness, modulus of elasticity and surface roughness.

Sample	P, [mN]	HU, [GPa]	H_{pl}, [GPa]	E,[GPa]	R_a, [µm]	R_z, [µm]	H_{pl}/E, [%]	H_{pl}^3/E^2, [%]
Substrate	500	2,069	2,188	141	0,20	1,31	1,552	0,053
(TiAlV)N/ TiO_x coating	50	13,513	20,601	205	0,25	2,01	10,05	20,80

The strength of hard coatings is due either to structural properties or the incorporated growth induced internal stresses. The fact that hardness increases for lower grain size is in accordance with other studies [1], where the increase in grain boundaries was shown to be the reason of slowing of the dislocations propagation and deformation mainly by grain boundary sliding. Contrary to what is claimed in [9] that layers based on (TiAl)N exhibit higher hardness up to 33 GPa (E=323 GPa) than TiN, the oxidized surface with porous structure shows even lower than conventional TiN hardness.

Since surface roughness increases after deposition of the coating (Table 1), the condition of the depth of the imprint of nanoindentation h as $h>R_z$ should be respect also. This increase is due to the presence of small droplets with different concentration and size and the existence of covered porous oxidized area (Figure 1), probably formed after nitrogen recombination during oxidation. It is known that the increased surface roughness and shape of the structures will determine osteocyte attachment against the implant surface and the strength of the bone to biomaterial contact.

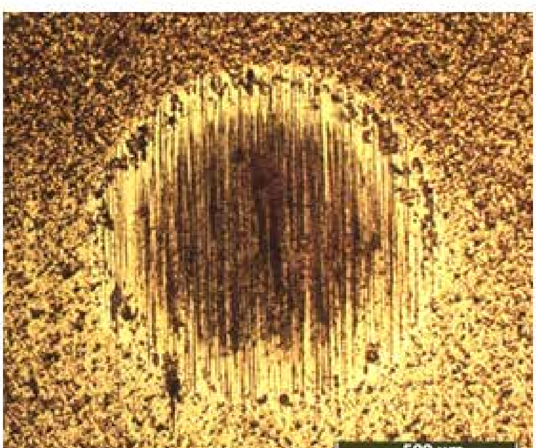

Figure 1. Microstructure of dimple after calotest wear of the (Ti,Al,V)N/TiO_x coating.

Both the hardness (H_{pl}) and the modulus of elasticity (E) of the material give more predictable results in ranking wear performance of engineering coatings. In this respect, a high H_{pl}/E and H_{pl}^3/E^2 ratios are desirable, since they imply a longer „elastic strain to failure" (i.e. improved resilience) and resistance to plastic deformation respectively [15]. The ratio H_{pl}/E was 2,8% for newer and 3,4% for older osteons [3]. As seen in Table 1, the same ratio for Ti substrate is below that of the bone. According to this fact, the substrate is inappropriate implant material for fretting and wear conditions. The improvement in the tribological properties (H_{pl}/E=10,05% and H_{pl}^3/E^2=20,8%) in comparison to bone and cpTi, the coating owes to its comparatively low modulus and high hardness because of its complex structure. It is necessary to note that these ratios present a probable wear resistance behavior only using static measurements.

For coatings, Young's modulus (E) depends on contact stress field, adhesion, coating delamination and detachment, layer thickness, structure and density of coating, residual stress [11]. According to the literature data, the Young's modulus of a TiN coating can vary in the range from 270 to 640 GPa [7] and for arc PVD TiN coating it is 380 GPa [9]. The coatings display only a (220) plane of reflection and therefore, the preferred orientation of cubic phase is the same. For NaCl structured (TiAlV)N the (220) plane is supposed to be less harder than the stiffest (111) plane.

The deposited (TiAlV)N coating has columnar morphology - typical of the film deposited at low temperature and low gas pressure during the process. The grain size is derived from the width of the diffraction peaks, (λ=1,937 Å, 2θ= 79,45° and β= 0,0297 rad), and it is 80,5 nm. Therefore, the strengthening based on dislocation mechanism becomes less distinct, but the grain boundary strength or the film packing density becomes more important [12].

The diagram of nanoindentation of the coatings at 50 mN load is shown on the Figure 2. Two zones are identified on the load curve: 1) zone A, which corresponds to a material with a porous structure and lower resistance against plastic deformation under compression, and 2) zone B, which corresponds to a dense material with a high resistance against plastic deformation under compression. In this case, zone A corresponds to the surface layer of TiO_x, while zone B corresponds to the underlying sublayer of (Ti,Al,V)N.

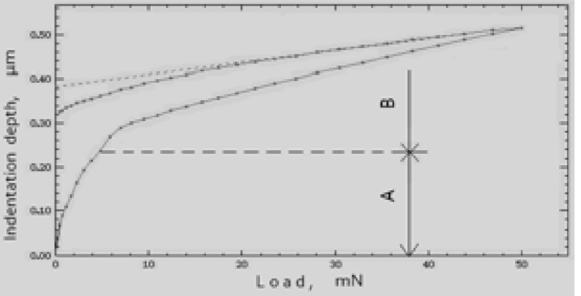

Figure 2. Experimental load-displacement curve for the (Ti,Al,V)N/TiO_x coating: A - TiO_x surface layer; B - (Ti,Al,V)N sublayer.

According to the curve, cracks in the layer do not appear. The small indentation area suggests that the materialis resistant to plastic deformation. There is not any failure during the indentation, so the coating is not sensitive to fine brittle failures of thin film surface.

If the thin fragile TiO_x coating is not sufficiently supported, it will fail at relatively low contact stresses because it cannot follow deformation of the sublayer or substrate ('egg-shell' effect). In addition, desirable compressive stresses that increase hardness and resistance to fatigue wear are displayed by PVD deposited coatings because of stress gradients arising from two competing stress generation mechanisms, namely growth-induced point defects (compressive stress) as a consequence of an atomic peeningand void formation (tensile stress) as a consequence of surface roughness and shadowing effects [5]. Then, with the introduction of (TiAlV)N sublayer the formation of lateral and radial cracks is suppressed. Furthermore, the applied negative bias voltage of substrate contributes to the compressive internal stresses in the layer [19]. The internal film stresses, chemical interactions, interdiffusion effects, imperfect contact, etc. contribute also to values of adhesion.

In scratch testing the critical load Lc_1 corresponds to the load inducing the first crack on the coating while Lc_2 corresponds to the load inducing the partial delamination of the coating [8]. The predetermined range of normal load was limited down deliberately in respect to the low substrate hardness. Detachment of the coating (Lc_2) up to 50 N and load inducing full delamination of the coating was not observed. Cohesion cracks at the scratch track bottom at the load of Lc_1 = 27,5 N was detected which did not affect integrity of the coating but the its surface uncovered and covered porous area. The coated specimen showed an excellent adhesion.

According to [16], implant Young's modulus equal to that of cortical bone (9 - 28,4G Pa [22]) is effective to inhibit the bone absorption when it is implanted. There are some other factors to be taken into account in order to make a valid comparison. First of all, as metals are denser than bone, the stresses in a bone made from titanium alloy would be about 1,3 times higher than that in a bone of the same weight [18]. Further, biological materials are capable of self-repair and thus improving their toughness. Therefore, in order to ensure long-term stability the implant materials should have higher strength and resistance to deformation than bone. Third, the bone itself is not isotropic, composite material. To reach down implant modulus like that of the bone, an artificial composite material, whose strength is difficult to estimate, is likely to be used [18]. Then, the point of combining low modulus with high strength for structural biomaterials that replace hard tissue is meaningless.

CONCLUSIONS

The results of this study prove that lower values of hardness and Young's modulus for (TiAlV)N and oxidized coating may be related to the internal structure and stresses of the deposited coat and morphology of grains. Lower modulus E of the multilayer coating results mostly from the grains size, their preferential orientation, loosened crystalline boundaries and concentration of elements across its thickness. It is clear that hard substrate phases of (TiAlV) N can provide good load supports for the phases of titanium oxides, which can greatly reduce their abrasive wear and adhesive wear for much longer time. Application of the proposed (TiAlV)N/TiO_x coating would be efficient in reducing wear and cracking and thus, improving mechanical biocompatibility of artificial joints, orthodontic implants, etc., made by β-titanium alloy for e.g..

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