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RESEARCH ARTICLE

Development of Biocompatible Coatings for Dental Implants Based on Transition Metal Nitrides

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Abstract

Nitrides are nitrogen (N) compounds with other chemical elements, in particular with transition metals. For transition metal nitrides, the main ones are properties such as homogeneity of the material of nitride products, high electrical conductivity, and high melting points, with hardness exceeding most other known materials. As experimental samples we used ready transition metals alloys from cylinders, 10 mm in diameter, and 20 mm in height. 10 cylinders for each alloy were used. Heating to the required temperatures was carried out using an induction heating furnace. Temperatures were measured with a DT model pyrometer, the measuring range of which ranges from -50 to + 110 °C, with an error of one tenth of a °C. Alloys were studied using electron microscopy, and the hardness of the resulting alloy was also measured. In addition to the samples of implants with a nitride coating, samples of cast products (implants) were produced. 10 samples of each type were made. The nitride film present almost doubled the hardness indices of metals and their alloys. The smallest wear out was observed for gold and platinum samples, the largest - for zirconium, titanium and nickel, 2-3 times more ($p \leq 0.05$). The presence of even the thinnest titanium nitride film changed these indicators, as a result of which the wear out level became even lower than that of gold ($p \leq 0.05$). The present nitride film prevents the formation of an adsorption layer. Such implants wear out will be slowed down in comparison with metal ones, but without a nitride film, on which an adsorption layer is formed. Along with the preference of titanium physical and chemical properties over other metals and their alloys, the deposition of a titanium nitride film is a necessary property to improve. Titanium has several advantages over other metals, including lower thermal conductivity and resistance to corrosion changes. Titanium nitride gives maximum hardness and maximum wear resistance. Nitride film implants acquire no damage; moreover, nitride spraying can also be used with other types of implants, for example, ceramics. The nitride film gives the metal base additional stability properties, creating a protective layer. The combined use of a titanium implant with titanium nitride spraying (layer thickness no more than 0.1 mm) increases the properties of hardness and wear resistance of implants.

Keywords: *Nitrogen (N) compounds; Transition metals alloys; Electrical conductivity; Dentistry; Dental implants.*

Introduction

Nitrides are compounds of nitrogen (N) with other chemical elements, in particular transition metals. The latter, having stability, include titanium (Ti^{4+}), iron (Fe^{3+}), zinc (Zn^{2+}). Other transition metals - like chromium (Cr^{2+}), manganese (Mn^{3+}), are unstable. The main properties for transition metal nitrides are properties such as homogeneity of the material of nitride products, high electrical conductivity, and high melting points, with hardness exceeding most other known materials [1, 5]. Obtaining nitrides is quite energy intensive, since it is associated with reactions of the corresponding metals in the presence of free nitrogen (N_2) or ammonia (NH_3) at high temperatures [6].There are the following modes under which such synthesis is carried out - combustion, production as a result of reactions in a plasmatron, and others- reduction of metal oxides, precipitation from gases, or by decomposition of salts (ammonia metal halides). All costs are more than offset by the benefits of using nitrides in various fields of human activity [7]. These include fire resistance, which is given to various parts and products, covering them with a nitride layer. In metallurgy, nitrides make components of hard alloys, as well as containers for melting and evaporating metals with a lower melting point (Al), or cutting edges for tools. One of the perspective applications for transition metal nitrides lies in an area that is not related to the main areas of application - in dentistry [8, 9]. From transition metal nitrides, it is possible to create coatings for dental implants [10]. This area is in development and the data and studies available are not enough to generalize the already known facts and develop new application technologies. All of the above has determined the relevance of this work. Implants must strictly correspond to a number of properties, due to which rejection reactions and active ion migration from the implant to the oral cavity will not be observed in connection with reactions with an aggressive environment (saliva).

For the successful functioning of the implant, porosity, a high degree of adhesion, as well as the presence of bioactivity, or, on the contrary, inertness and the absence of a pronounced immune response of the body to the implant are mandatory [11, 12]. On the surface of the implant, it is necessary to form a coating that meets such requirements as the necessary structure of the surface layer and its heterogeneity with respect to the internal ones. All this implies a complex set of interactions between specialists in the field of medicine, immunology, engineers and chemists. The properties of certain types of dental implants can have a negative impact on human health, including pathologies in the field of oncology, as well as disorders associated with galvanic pathology. The goal of our work is to develop biocompatible coatings based on transition metal nitrides for implants in dentistry. In addition, we have compared the chemical, physical and biological properties of transition metal nitrides with those of other materials used in the manufacture of implants in dentistry.

Material and Methods

The work was carried out in 2017 at the laboratories of the Sechenov First Moscow State Medical University (Sechenov University).As experimental samples used finished alloys of transition metals from cylinders, 10 mm in diameter, and 20 mm in height. Such cylinders are necessary for microscopic tests. 10 cylinders were used for each alloy. The composition of the alloy was recognized using a fluorescence X-ray method (X-ray spectral analysis) using a spectrometer. Heating to the required temperatures was carried out using an induction heating furnace.

Temperatures were measured with a pyrometer of the DT model, whose range varies from -50 to +1100°C, with an error of one tenth of a degree. The studied coatings were applied to the polished and cleaned surface of the studied alloys by plasma-chemical deposition methods. Additionally, the resulting coatings were studied using electron microscopy, and the hardness of the resulting alloy was also measured. The second part of our work included the manufacture of dental implant samples. In addition to samples of implants with a nitride coating, those were produced that have been used for a long time in dentistry, in particular, products from precious metals (gold). Quantitative indicators of dental cast products are given in Table 1 out of 10 samples of each type.

Table 1: The composition and quantitative characteristics of the materials the implants are made from

Alloy composition	Quantitative characteristics of the coating, % of each of the elements	The presence (+) or absence (-) of a nitride coating
Nickel-titanium	50+50	+
Nickel (Chrome + Molybdenum)	59 (25+15)	-
Titanium	100	+
Zirconium	100	-
Titanium (aluminum)	92 (4-6)	+
Titanium (Aluminum + Molybdenum)	85 (6+4)	-
Gold (Platinum)	87 (11)	-
Nickel (Chrome + Molybdenum)	61 (23+6)	-

We used titanium nitride as a nitride coating, which was applied to 3 types of dental implants out of 8 (Table 1). Titanium is selected as a transition metal, which has a high melting point and is chemically inactive. In addition, titanium has a combination of properties such as strength and lightness. According to some reports, the presence of titanium and alloys with its base, as well as niobium and platinum in the body can be unlimited for a long time, comparable to the life expectancy of an individual. For other metals, such as nickel, tungsten, copper and cobalt, being in the body can cause toxic processes. Finally, for iron, molybdenum, aluminum, silver and gold, a short stay in the body is possible without visible consequences. Anticorrosion properties, resistance to aggressive media (immersion in a solution simulating saliva at 36 °C in composition, holding for 30 minutes), as well as changes in the stationary potentials of metals and their alloys for implants with and without coating were tested. In this case, two electrodes were used; each of the electrodes was alternately passed through a model solution until it came into contact with the studied metal or its alloy.

Next, one of the electrodes was removed and dried. After that, a furrow was applied to this electrode, which should be similar to a mechanical effect. The width and length of the furrow in all samples did not differ and amounted to 2.5 by 0.5 mm, respectively. To assess the effect of slag in each of the 20 samples consisting of ceramics, a hole with a diameter of 5 mm was drilled. The surface of the hole was covered with a layer of titanium nitride. The thickness of the titanium nitride layer is 0.01 mm. The hole imitated carious changes that violate the integrity of the tooth and lead to its destruction. Slag consisting of oxides (silicon, aluminum, iron, manganese, calcium, magnesium, sodium, potassium, titanium, chromium and phosphorus) was fed into the hole. The ratio of oxides in the slag ranged from 0.05 to 30%. Thus, obtained experimental sample was placed in a furnace, where for half an hour it was kept at maximum heating of 1000°C. Next, an incision was made of the sample and its microscopic examination. We selected slag due to the fact that it is the most chemically aggressive medium. The above differences are significant at $p \leq 0.05$. For data processing used the program Past v. 3.0 the significance of differences between the characters was checked by applying the Fisher two-sample t-test for independent samples. In the tables, the average values are given together with the average error.

Results

Tests for Hardness and Wear Resistance

The tests for hardness and wear resistance performed on the prototypes showed differing results (Table 2). The bulk of the alloys have the same hardness as tooth enamel. According to the data, tooth enamel has hardness indices in the range of 3.3-4.3 GPa. Titanium and its alloys have close values to tooth enamel. Softer than enamel, indicators have an alloy of gold and platinum, zirconium. Nickel has the maximum hardness.

Table 2: Indicators of hardness and wear resistance of metals and their alloys, taking into account and without taking into account the presence of a nitride film

Alloy composition	Hardness values (GPa)	Hardness values taking into account titanium nitride film (GPa)	Sample Wear (mm^3)	Wear based on titanium nitride film (mm^3)
Nickel-titanium*	4.9±0.3	8.3±0.5	$5.010*10^{-4}$	$1.100*10^{-4}$
Nickel (Chrome+Molybdenum)	4.8±0.2	-	$6.636*10^{-6}$	-
Titanium*	4.1±0.2	7.9±0.4	$8.309*10^{-4}$	$1.010*10^{-4}$
Zirconium	2.6±0.6	-	$8.390*10^{-4}$	-
Titanium (Aluminum)*	5.0±0.4	8.1±0.3	$3.367*10^{-4}$	$1.150*10^{-4}$
Titanium (Aluminum+Molybdenum)	5.1±0.3	-	$3.590*10^{-4}$	-
Gold (Platinum)	2.7±0.3	-	$2.497*10^{-7}$	-
Nickel (Chrome+Molybdenum)	7.9±0.7	-	$7.390*10^{-6}$	-

* - titanium nitride film coated alloys

On the other hand, the presence of a nitride film almost doubled the hardness indices of metals and their alloys (Table 2, at $p \leq 0.05$). The use of a nitride film, thus, increases the hardness of the implants. Wear resistance is the other side of the parameters important for implants. Depreciation leads to irreversible changes in the surface structure of implants and a possible pathology of galvanic origin. The smallest wear, as shown by our studies, was observed for samples of gold and platinum, the largest -for zirconium, titanium and nickel, 2-3 times more ($p \leq 0.05$).

The presence of even the thinnest film of titanium nitride changed these indicators, as a result of which the level of wear became even lower than that of gold ($p \leq 0.05$). Thus, titanium nitride films give implants maximum hardness and minimum wear, which gives durability to implants.

Corrosion and Abrasive Tests of Various Types of Dental Implants

Being in the oral cavity, dental implants are subjected to two types of effects - corrosion and abrasion. Table 3 shows the potentials of metals and their alloys after a current measurement in a system with an updated surface of one of the two electrodes.

Table 3: The potential values of metals and their alloys

Alloy composition	Potential values (given on a standard hydrogen scale)	Values excluding titanium nitride film
Nickel-titanium*	+0.015	+0.130
Nickel (Chrome+Molybdenum)	+0.139	-
Titanium*	+0.014	+0.052
Zirconium	-0.043	-
Titanium (Aluminum)*	+0.015	+0.047
Titanium (Aluminum+Molybdenum)	+0.061	-
Gold (Platinum)	+0.301	-
Nickel (Chrome+Molybdenum)	+0.143	-

* - titanium nitride film coated alloys

As can be seen from the data presented, the presence of the thinnest layer of a titanium nitride film completely changes the properties of conductivity, despite the fact that some of the metals or their alloys have high indices. For example, the performance of a nickel-titanium alloy can differ by 9 times between an alloy and an alloy with a nitride film, and by 3 times for a titanium-aluminum alloy (at $p \leq 0.05$). With an increase in the exposure time to 2 hours, in metals without nitride coatings, the conductivity changes in the direction of shear to positive values.

The differences are significant and the indicators shift relative to those given in Table 3 to 25%. For zirconium and metals with a nitride film, no significant differences were recorded. The changes that have occurred in metals are associated with the formation of a thin adsorption layer on them. This layer prevents further dissolution (electrochemical nature) of metals and their alloys. From this we can conclude that the presence of a nitride film prevents the formation of an adsorption layer. The wear of such implants will be slowed down compared to those on which the adsorption layer has formed.

The Consequences of the Introduction of Slag into Ceramics

Visible damage to the samples was not noted. At the boundary between the slag melt, titanium nitride and ceramics, a layer is formed that varies in thickness, from 40 to 90 microns. The zone of direct contact between the slag and ceramics was absent.

In this case, titanium nitride played the role of a protective layer that protects the ceramic part of the implant from destructive effects. The studies using optical and electron microscopes showed the absence of grains (globules) in this zone. In addition, it was found that the nitride film reduced the slag to metal, thereby creating additional (in addition to nitride) protection. Such protection is doubly able to resist corrosion of the ceramic part of the implant.

Discussion

The use of titanium in dental prosthetics and implants. Various metals and their alloys are known to have varying degrees of application in dental products. For example, gold is best used for inlays and on lays, crowns and bridges, silver are suitable for use in crowns and bridges [13, 14]. Cobalt-chromium alloy is most often used for crowns, bridges, implants and partial dentures, while nickel-chromium is suitable only for crowns and bridges. Iron is used to create orthodontic appliances. Finally, titanium is suitable for crowns, bridges, and implants [15]. Therefore, no universal metals or their alloys exist [16]. At the same time, some of them are toxic to the body, as mentioned above.

Therefore, titanium and its alloys are almost ideally suited for the creation and implants implementation [17, 18]. The introduction of implants from metals and their alloys, as shown in a number of works, can cause pathological changes of galvanic nature in 10-30% of patients. In these studies, the results were obtained for patients with fixed dentures, which include implants [19, 20].

The more implants in the patient's oral cavity, the greater the amount of metal cations contained in saliva. All this leads to the development of the galvanic syndrome. Out of the metals and their alloys that we examined and tested, the lowest indicators for the possibility of the development of the galvanic syndrome are titanium and its alloys [21, 22]. Along with the preference for the physical and chemical properties of titanium over other metals and their alloys, the necessary property to improve is the deposition of a titanium nitride film. Titanium has several advantages compared with other metals - lower thermal conductivity and resistance to corrosion changes [23]. Titanium is known to be resistant to dissolution in acids, alkalis, and various aggressive media of biological origin [24].

Today, in some EU countries, for example in Germany, all implants are made of titanium. Most prosthetic joints and other orthopedic products are also made on the basis of titanium or its alloys [25, 26]. The most important property that should be considered for implants is the adhesion of bone cells, osteoblasts. Titanium and its alloys are proved to have high adhesion, i.e., are most densely held by osteoblasts [27, 28]. A titanium implant will quickly become overgrown with bone tissue. In addition, there is evidence of bactericidal properties of titanium, similar in effect to silver ions [29]. Studies on titanium nitride with the addition of various alloying metals to the melt showed that its hardness increases by 10-15% [30, 31]. This is due to changes at the microscopic level. The size of grains (globules) is reduced by a factor of 2, from 10 nm to 5 nm [32]. These properties are stored up to 1000°C. Starting at a temperature of 1100°C, the nitride hardness begins to decline [33]. Titanium nitride gives maximum hardness and maximum wear resistance. Nitride film implants have no damage; moreover, nitride spraying can also be used with other types of implants, for example, ceramics. The nitride film gives the metal base additional stability properties, creating a protective layer.

Conclusions

The combined use of a titanium implant with titanium nitride spraying (layer thickness not more than 0.1 mm) increases the properties of hardness and wear resistance of implants.

References

1. Banaszek K, Januszewicz B, Wołowiec E, Klimek L (2015a) Complex XRD and XRF characterization of TiN-TiCN-TiC surface coatings for medical applications. Solid State Phenom, 225: 159-168.
2. Banaszek K, Pietnicki K, Klimek L (2015b) Effect of carbon and nitrogen content in Ti(C, N) coatings on selected mechanical properties. Met. Form, 26: 33-45.
3. Banaszek K, Klimek L (2015) Wettability and surface free energy of Ti(C, N) coatings on nickel-based casting prosthetic alloys. Arch. Foundry Eng., 15: 11-16.
4. Banaszek K, Klimek L, Zgorzynska E, Swarzynska A, Walczewska A (2018) Cytotoxicity of titanium carbonitride coatings for prostodontic alloys with different amounts of carbon and nitrogen. Biomed. Mater., 13: 045-003.
5. Pawlak R, Tomczyk M, Walczak M (2012) The favorable and unfavorable effects of oxide and intermetallic phases in conductive materials using laser micro technologies. Materials Science and Engineering: B, 177(15): 1273-1280.
6. Pietrzyk B, Miszczak S, Szymanowski H, Kucharski D (2013) Plasma enhanced aerosol-gel deposition of Al2O3 coatings. Journal of the European Ceramic Society, 33(12): 2341-2346.
7. Beck KA, Sarantopoulos DM, Kawashima I, Berzins DW (2012) Elemental release from CoCr and NiCr alloys containing palladium. J. Prosthodont, 21: 88-93.
8. De Viteri VS, Barandika MG, de Gopegui UR, Bayón R, Zubizarreta C, Fernández X, Agullo-Rueda F (2012) Characterization of Ti-CN coatings deposited on Ti6Al4V for biomedical applications. Journal of inorganic biochemistry, 117: 359-366.
9. De Viteri VS, Barandika G, Bayón R, Fernández X, Ciarsolo I, Igartua A, Peremarch CPJ (2016) Development of Ti-C-N coatings with improved tribological behavior and antibacterial properties. Journal of the mechanical behavior of biomedical materials, 55: 75-86.

10. Serro AP, Completo C, Colaço R, Dos Santos F, Da Silva CL, Cabral JMS, Saramago B (2009) A comparative study of titanium nitrides, TiN, TiNbN and TiCN, as coatings for biomedical applications. Surface and Coatings Technology, 203(24): 3701-3707.
11. Almazdi AA, Khajah HM, Monaco EA Jr, Kim H (2012) Applying microwave technology to sintering dental zirconia. J. Prosthet. Dent, 108: 304-309.
12. Banaszek K, Wiktorowska-Owczarek A, Kowalczyk E, Klimek L (2016) Possibilities of applying Ti (C, N) coatings on prosthetic elements-research with the use of human endothelial cells. Acta Bioeng. Biomech., 18: 119-126.
13. Bociaga D, Mitura K (2008) Biomedical effect of tissue contact with metallic material used for body piercing modified by DLC coatings. Diam. Relat. Mater, 17: 1410-1415.
14. Bociaga D, Jakubowski W, Komorowski P, Sobczyk-Guzenda A, Jedrzejczak A, Batory D, Olejnik A (2016) Surface characterization and biological evaluation of silver-incorporated DLC coatings fabricated by hybrid RF PACVD/MS method. Mater. Sci. Eng. C, 63: 462-474.
15. Miyazaki T, Hotta Y (2011) CAD/CAM systems available for the fabrication of crown and bridge restorations. Australian dental journal, 56: 97-106.
16. Cicciù M, Fiorillo L, Herford AS, Crimi S, Bianchi A, D'Amico C, Cervino G (2019) Bioactive Titanium Surfaces: Interactions of Eukaryotic and Prokaryotic Cells of Nano Devices Applied to Dental Practice. Biomedicines, 7(1): 12.
17. Brama M, Rhodes N, Hunt J, Ricci A, Teghil R, Migliaccio S, De Maria G (2007) Effect of titanium carbide coating on the osseointegration response in vitro and in vivo. Biomaterials, 28(4): 595-608.
18. Näpänkangas R, Raustia A (2011) An 18-year retrospective analysis of treatment outcomes with metal-ceramic fixed partial dentures. International Journal of Prosthodontics, 24: 4.
19. Raap U, Stiesch M, Reh H, Kapp A, Werfel T (2009) Investigation of contact allergy to dental metals in 206 patients. Contact Dermatitis, 60(6): 339-343.
20. Drago C, Howell K (2012) Concepts for designing and fabricating metal implant frameworks for hybrid implant prostheses. Journal of Prosthodontics: Implant, Esthetic and Reconstructive Dentistry, 21(5): 413-424.
21. Noda M, Wataha JC, Lockwood PE, Volkmann KR, Kaga M, Sano H (2002) Low- dose, long- term exposures of dental material components alter human monocyte metabolism. J. Biomed. Mater. Res, 62: 237-243.
22. Jang HW, Lee HJ, Ha JY, Kim KH, Kwon TY (2011) Surface characteristics and osteoblast cell response on TiN-and TiAlN-coated Ti implant. Biomedical Engineering Letters, 1(2): 99-107.
23. Małkiewicz K, Sztogryn M, Mikulewicz M, Wielgus A, Kamiński J, Wierzchoń T (2018) Comparative assessment of the corrosion process of orthodontic archwires made of stainless steel, titanium-molybdenum and nickel–titanium alloys. Archives of Civil and Mechanical Engineering, 18(3): 941-947.
24. Krzak-Ro´s J, Filipiak J, Pezowicz C, Baszczuk A, Miller M, Kowalski M, Będziński R (2009) The effect of substrate roughness on the surface structure of TiO2, SiO2, and doped thin films prepared by the sol-gel method. Acta of Bioengineering and Biomechanics, 11(2): 21-29.
25. Januszewicz B, Klimek L (2004) Investigation of TiCN coatings on steel substrates deposited by means of low-pressure cathode ARC technique. Acta Metallurgica Slovaca, 10: 926-929.
26. Heintze SD, Rousson V (2010) Survival of zirconia-and metal-supported fixed dental prostheses: a systematic review. International Journal of Prosthodontics, 23(6): 493-502.
27. Rylska D, Sokołowski J, Klimek L (2004) Corrosion resistance investigations of prosthetic dental alloys coated by TiN. Annals of Transplantation, 9(1A): 104-108.
28. Galo R, Ribeiro RF, Rodrigues RCS, Rocha LA, Mattos MDGCD (2012) Effects of chemical composition on the corrosion of dental alloys. Brazilian dental journal, 23(2): 141-148.
29. Faccioni F, Franceschetti P, Cerpelloni M, Fracasso ME (2003) In vivo study on metal

release from fixed orthodontic appliances and DNA damage in oral mucosa cells. American Journal of Orthodontics and Dentofacial Orthopedics, 124(6): 687-693.

30. Szymanowski H, Sobczyk A, Gazicki-Lipman M, Jakubowski W, Klimek L (2005) Plasma enhanced CVD deposition of titanium oxide for biomedical applications. Surface and coatings technology, 200(1-4): 1036-1040.
31. Chien CC, Liu KT, Duh JG, Chang KW, Chung KH (2008) Effect of nitride film coatings on cell compatibility. Dental materials, 24(7): 986-993.
32. Von Steyern Vult P (2005) All-ceramic fixed partial dentures. Studies on aluminum oxide-and zirconium dioxide-based ceramic systems. Swedish dental journal. Supplement, (173), 1-69.
33. Wang G, Zreiqat H (2010) Functional coatings or films for hard-tissue applications. Materials, 3(7): 3994-4050.