



Multilayer and Nanocomposite Hard Coatings for Biomedical Applications

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Advanced hard coating concepts like multilayer coatings, multicomponent solution hardened layer materials, new metastable layer materials, nanocrystalline layer materials or superlattice films become increasingly important for wear protection under extreme and complex loads. Among these advanced coatings, the multilayer concepts seems to be the most versatile and promising with respect to properties and performance in almost all the fields of application. Nanostructured multilayer coatings exhibit outstanding physical, mechanical, and chemical properties, opening a range of new applications in high technologies. These outstanding properties are due to the interface and nanoscale effects associated with structural peculiarities of nanostructured coatings where the volume fraction of the interfacial phase is extremely high, and crystalline size does not exceed 100 nm. Multilayers are extensively used in semiconductor, optical, and metallurgy industries and are becoming of increasing importance in areas such as magnetic recording, superconductors, and, lately, wear- and corrosion-protective coatings.

Titanium and its alloys are widely applied in various fields of human activity including medicine. This is still the most commonly used material for surgical tools and biological devices, like implants and endoprosthesis. The main advantages of titanium-based materials in medical applications is their good biocompatibility, low density, high level of mechanical properties and corrosion resistance. However, one of the important features limiting the application of this material in medicine is its relatively low wear resistance, leading to the release of the material elements into the surrounding cells or tissues in a biological environment. Most processes proceeding in the human body occur at surfaces and interfaces of implant material. The main effective method for overcoming the above mentioned limitation therefore concerns a surface modification, which would improve biological function, with a hard coating. Nowadays, the possibility to modify and control the surface wettability of biological materials has attracted significant scientific and technological interest. For biological systems the nature of hydrophobic and hydration forces plays a key role on the mediation of solute adsorption and cell adhesion.

TiN is very hard and has excellent wear and corrosion resistance. It also has a high chemical and thermodynamic stability and significant metallic properties such as a bright yellow and excellent conductivity. TiN films are widely used in a variety of tools and frictional resistance applications in order to increase the device life time. It can also be used as a barrier layer between the silicon and metal films. The Ti/TiN multilayer films and related hard coatings can be deposited by RF magnetron sputtering, dc magnetron sputtering, laser ablation, pulsed laser deposition, hollow cathode ion plating, vacuum arc and arc ion plating. Ti/TiN multilayered coatings deposited by a reactive magnetron sputtering have found many virtues, e.g. higher hardness, toughness, wear resistance and good adhesion strength.

The structural, mechanical, corrosion properties and biocompatibility of TiN/TiAlN, TiN/NbN, TiN/VN multilayer and Ti-Si-N nanocomposite coatings are the important hard coatings for biomedical application. The lower friction coefficient and wear rate observed for the multilayer coated sample indicated that they have better wear resistance. Multilayer coatings show better hemocompatibility than single layer and bare AISI 316LSS substrates. The attachment of

bacteria on multilayer coatings was found to be very minimum and without colonization. The multilayer coated 316L surfaces showed a significant reduction of the presence of bacteria, and this fact could probably be important in the decrease of the inflammation of the peri-implant soft tissues. Potentiodynamic polarization study is an important too, which showed that the positive shift in E_{corr} and decrease in I_{corr} values for multilayer coating. This signifies that it exhibits higher corrosion resistance than single layer and bare substrate in simulated body fluid. It may be proposed that by using the multilayer coated 316L SS as a human body implant, improvement of corrosion resistance as an indication of biocompatibility could be obtained. To improve the osseointegration between the implant surface and tissue, a top layer of hydroxyapatite can be coated.

Recently various surface coating technologies have been employed to enhance the important functional properties such as lubricity, biocompatibility and antimicrobial effect for medical devices and surgical tools. Commercially pure titanium (CP-Ti) and Ti-6Al-4V, remain the two dominant titanium alloys used in implants. The stability of the oxide layer formed on CP Ti (and consequently its high corrosion resistance) and its relatively higher ductility (i.e., the ability to be cold worked), compared to Ti-6Al-4V, have led to the use of CP Ti in porous coatings (e.g., fiber metal) and Total Joint Arthroplasty (TJA) components. Generally, joint replacement components (i.e., TJA systems) are made of Ti-6Al-4V rather than CP-Ti because of its superior mechanical properties. In recent years metallic oxynitrides have become interesting research materials because of their remarkable optical and electronic properties, mechanical behavior, as well as chemical stability and good adhesion to polymers, anti-reflective, decorative and/or diffusion barrier coating for polymer components. In recent studies, they revealed properties common to both metallic TiN and semi-conducting TiO_2 compounds. Titanium oxide film is a widely used biocompatible material; therefore modification of wetting behavior is of great importance for its biomedical application. TiN coatings, on the contrary, are mostly used as protective and decorative coatings because of their extreme wear resistance and aesthetic golden color. In addition, TiN coatings serve as diffusion barriers due to their thermodynamic stability. Indeed titanium oxynitrides exhibit the combined properties of metallic oxides (color, optical properties) and nitrides (hardness, wear resistance). At present, interests in titanium oxynitride films has increased and have been extensively studied due to their improved physical and chemical properties, which mainly depend

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on their N/O ratio. The wettability studies to determine hydrophilic or hydrophobic nature of titanium oxynitride film is the area that is unexplored and not much literature has been found regarding the investigation of this property so far. TiN_xO_y films are the representative transition metal oxynitrides that can be deposited onto different substrates by various chemical vapor deposition (CVD) and physical vapor deposition (PVD) techniques with a tuneable N_yO ratio and consequently, with a wide range of physicochemical properties. Reactive magnetron sputtering is specially an attractive process to deposit TiON films because of its several intrinsic advantages over CVD and PECVD process. The main advantages include low-temperature deposition, large area deposition and use of non-toxic gas. Sputtering of a titanium target

in a mixed working gas (O₂ and N₂) or in a reactive gas atmosphere can be also used to obtain a tuneable N/O ratio in the films.

From the above facts and the salient materials properties of the hard coating discussed, it can be largely concluded that a thin single or multilayers of hard coatings with nano grains deposited on metal surface implants favorable physicochemical and mechanochemical characteristics such as corrosion resistance, wear resistance and good adhesion while retaining the durability and structural benefits of the metal. This field of research provides lot of scope for the materials scientists, and biomedical experts, which has large inter disciplinary research future.

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