Abstract

Titanium and its alloys are regarded as exceptional biomaterials, extensively used in several prosthetic implant applications owing to their excellent biocompatibility, lightweight, high specific strength, and corrosion resistance. Nevertheless, these Ti alloys can experience significant wear owing to their low hardness, poor tribological performance, and limited corrosion resistance in complex biological environments.

This thesis work emphasizes the development of advanced hard, wear-resistant biocompatible coatings on the Ti-6Al-4V alloy to improve its functional characteristics, hardness, elastic modulus, wear resistance, corrosion resistance, and biocompatibility. Titanium and Zirconium-based coatings with different architectures like monolayer (TiN and ZrN), ceramic-ceramic multilayer (TiN/ZrN), and ceramic-metal composite multilayer (TiN/Zr and ZrN/Zr) have been developed through various physical vapor deposition (PVD) techniques, i.e., Cathodic arc evaporation (CAE), Magnetron sputtering (MS), and hybrid PVD (CAE+MS). Initially, TiN monolayer was developed by cathodic arc evaporation (CAE), and its mechanical and tribological properties have been enhanced by optimizing the process parameters of CAE. Furthermore, ZrN monolayer has been developed by magnetron sputtering (MS), and its enhanced functional properties have been achieved through the optimized process parameters of magnetron sputtering. The comprehensive microstructural, elemental, phase evaluation, and topographical analysis have been carried out by field emission scanning electron microscopy (FESEM), transmission scanning electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction analysis (XRD), and atomic force microscopy (AFM). Furthermore, TiN/ZrN multilayer coatings have been developed through hybrid PVD (CAE+MS). A detailed comparative study has been conducted on monolayer and multilayer coatings, based on performance evaluations of mechanical properties, wear resistance, and

corrosion resistance. Mechanical properties such as hardness (H), elastic modulus (E_r), H/E_r, and H^3/E_r^2 have been analyzed through nanoindentation test. Tribological properties, including friction coefficient and wear rate, have been evaluated under two different wear configurations, i.e., unidirectional linear reciprocation (using a multifunction tribometer) and cross-shear motion (using the prosthetic biotribometer). Cross-shear motion represents a close mimic of the actual implant motion kinematics (specifically for hip implant) according to ASTM F732 standard. Corrosion resistance has been studied using a potentiodynamic polarization test.

TiN/ZrN multilayer coatings exhibited a significant improvement in the hardness compared to monolayer coatings of TiN and ZrN. However, there was no substantial improvement observed in wear resistance performance due to the delamination and brittle fracture of the ceramic-ceramic multilayer coating.

Metal-ceramic composite multilayer coatings (TiN/Zr and ZrN/Zr) have been developed, and their relationship regarding structure and properties has been analyzed. These coatings demonstrated a significant improvement in wear resistance under linear and cross-shear wear conditions. The adhesion strength evaluated through the scratch test showed noticeable improvement in the adhesion of the coating with the Ti alloy substrate. This is attributed to the effect of inserting metallic bilayers alternating with ceramic layers, which in turn worked as stress-absorbing layers. These layers have provided sufficient toughness to the composite coatings. Furthermore, the biocompatibility of the developed ceramic-metal composite coatings has been studied for cell viability using an in vitro MTT assay (3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) with mouse fibroblast NIH/3T3 cell lines. Coated Ti-6Al-4V alloy exhibited significant improvement in cell viability compared to bare Ti-6Al-4V alloy. Coated surfaces show 2 to 3 times increase in cell viability with increased optical density compared to bare Ti-6Al-4V alloy. This is attributed to the altered surface

topography and chemistry of the coated surfaces, which provide a more favourable environment for cellular attachment and proliferation.

Keywords: Ti-Zr-based coating, Composite multilayer, Hybrid PVD, Mechanical properties, Bio-tribology, Corrosion resistance, Cell viability