Abstract

Titanium and its alloys are widely used as bio-implant due to their high strength to weight ratio, low young's modulus (relatively close to the human bone) and good corrosion resistance in physiological environment. In addition, Ti and its alloy have strong affinity towards oxygen and therefore, they form a thin (usually in the 3-10 nm range), passive and protective titanium oxide layer on the surface. However, the stoichiometrically defective nature of surface oxide leads to the poor stability of native oxide in the physiological environment. In addition, titanium and its alloys possess a poor wear resistance property which causes accumulation of worn debris in the joint region. Wear and bioactivity are surface dependent properties which may be improved by tailoring the surface microstructure and/or composition of the surface. In the present investigation, extensive studies have been undertaken to tailor the surface properties of Ti-6Al-4V for bio-implant application by (a) engineering surface topography by laser surface texturing, (b) developing TiO_2 coating and hydroxyapatite (HA) based composite coating with incorporation of TiO_2 and ZrO_2 by plasma spraying and studying the effect of post spray heat treatment on the characteristics and properties of the surface, and (c) developing thick oxide based bioactive coating mainly of TiO_2 on Ti-6Al-4V substrate by electro-chemical (plasma electrolytic oxidation) route.

Laser surface texturing of Ti-6Al-4V has been carried out by ArF excimer laser at a wavelength of 193 nm with a pulse length of 5 ns in air. Followed by surface texturing, a detailed investigation has been undertaken to understand the effect of texture morphology and the associated surface characteristics on the wear, corrosion and bio-activity of the surface. Laser surface texturing develops uniform, defect free and periodic surface patterns

with dimples and linear geometries. Microstructure shows the refinement of grain along with presence of α, β, rutile, anatase and few Ti_2O_3 phases. There is a significant improvement in nano-hardness (4 GPa for linear textured surface and 6 GPa for dimple textured surface as compared to 2 GPa for as-received Ti-6Al-4V substrate), and young's modulus (139 GPa for linear textured surface and 148 GPa for dimple textured surface as compared to 117 GPa for as-received Ti-6Al-4V substrate), in the textured surface. There is marginal improvement in wear resistance of laser textured surface as compared to as-received substrate. The total surface energy is decreased due to linear texturing (29.6 mN/m) and increased due to dimple texturing (67.6 mN/m) as compared to sand blasted (47 mN/m) and as-received Ti–6Al–4V (37 mN/m) substrate. The polar component of the surface energy is significantly higher in sand blasted surface (31.9 mN/m) as compared to linear textured surface (27 mN/m), dimple textured (9.9 mN/m) surface and as-received Ti-6Al-4V (11.3 mN/m) substrate. In contrast, the dispersive component of the surface energy is significant higher in dimple textured surface (58 mN/m) as compared to linear textured surface (1.98 mN/m), sand blasted (15.2 mN/m) and as-received Ti-6Al-4V (26.4 mN/m) substrate. There is a significant improvement in bioactivity in terms of calcium phosphate deposition (33% in linear textured, 27% in dimple textured as compared to 23% of sand blasted and 20% in as-received Ti-6Al-4V substrate) after 7 days of immersion in Hank's solution. A comparable cell viability of laser textured surface is observed as that of as-received Ti-6Al-4V. A detailed cell attachment study shows that cell adherence is preferred along ridges and corners and is less in the dimple textured surface as compared to as-received one. In linear textured surface, cells are preferentially adhered along the direction of texturing.

Plasma spraying of TiO_2 and HA based composite (HA+50 wt. %TiO_2 and HA+10 wt.% ZrO_2) coatings have been carried out on Ti-6Al-4V substrate at an applied voltage of 42 V, and arc current of 900 Amps. Followed by spraying, heat treatment has been carried out at 550°C (for 2 hrs.) for TiO_2 coating, at 650°C (for 2 hrs.) for HA +50 wt.% TiO_2 coating, and at 750 °C (for 2 hrs.) for HA+10 wt.% ZrO_2 coating. Plasma spray deposited surface shows the presence of porosity and un-melted particles on the surface, the area fraction of which decreases after heat treatment. X-ray diffraction analysis shows the phase transformation from anatase (in precursor powder) to rutile (in as-sprayed coating and the same after heat treatment) in the TiO_2 coated surface. HA based composite coating shows decomposition of HA and formation of $CaTiO_3$ phase in HA + 50 wt.% TiO_2 composite coating and presence of $CaZrO_3$ phase in the HA+10 wt.% ZrO_2 composite coating. There is an improvement in hardness after heat treatment as compared to as-sprayed coating (from 4.6 GPa to 4.8 GPa in TiO_2 coating, 2.15 GPa to 2.2 GPa in HA+50 wt.% TiO_2 coating and 1.1 GPa to 2.3 GPa in HA + 10 wt.% ZrO_2 coating). A significant improvement in wear resistance and corrosion resistance is observed in the coating after heat treatment as compared to as sprayed coating. Bioactivity in terms of calcium phosphate deposition is higher in all coatings (in both as-sprayed state and the same after heat treatment) as compared to as-received Ti-6Al-4V and as sprayed coating offers a superior behavior as compared to the same after heat treatment.

Finally, plasma electrolytic oxidation (PEO) has been applied to develop oxide coating on Ti-6Al-4V substrate at an applied voltage of 430 V (under constant voltage mode) with a current limitation of 1 A (in the ramp-up to final voltage) for 10 minutes duration. There is formation of a porous (35% porosity) oxide coating with 150 μm thicknesses and consisting of anatase, rutile, calcium phosphate and SiO_2 phases on the surface of Ti-6Al-

4V substrate. A significant improvement in hardness (from 2 ± 0.4 GPa for as-received Ti-6Al-4V to 8 ± 0.5 GPa for PEO treated surface), wear resistance in terms of decrease in wear depth (from 100 μm for as-received Ti-6Al-4V to 23 μm for PEO treated surface) and corrosion resistance in terms of decrease in corrosion rate (from 1.23×10^{-1} mm/year for as received to 5.76×10^{-3} mm/year for PEO treated surface) of PEO treated surface is observed. There is also an improvement in wettability of PEO treated sample in terms of decrease in contact angle (from 60^{o} for as-received Ti-6Al-4V to 45^{o} in PEO treated surface). The bio-activity of the PEO treated surface has been improved as compared to as-received Ti-6Al-4V substrate.

This thesis is divided into five chapters. Chapter 1 contains the brief introduction of the present work. Chapter 2 provides the critical literature review of the reported work. Chapter 3 describes the experimental techniques used for (a) surface modification and coating, (b) the tools and techniques applied for characterization, and the techniques used for evaluation of (c) mechanical properties, (d) corrosion resistance, (e) bioactivity behavior in Hank's Solution, and (f) wettability. Chapter 4 illustrates the results and discussions pertaining to as-received and surface tailored Ti-6Al-4V alloy. Finally, Chapter 5 shows the comparative studies on the results obtained in the present study, major conclusions drawn and its future scope of application.

Keywords: Ti-6Al-4V, Laser surface texturing, Plasma Spraying, Plasma electrolytic oxidation (PEO), Nano-indentation, Wear, Corrosion, Bioactivity, Wettability, Surface Energy.