Abstract

Ti6Al4V alloy (Ti - 6wt.% Al - 4wt%. V) is an important category of α +β titanium alloy with low density (4.43 g/cm^3), high strength-to-weight ratio, and low Young's modulus, as a result of which it has a wide range of applications as components/devices for bioimplant applications. Prolonged exposure of Ti6Al4V-based implants (used for hard tissue replacement) causes progressive removal of material due to chemical degradation because of corrosion and mechanochemical degradation because of its constant interaction with human bone under fretting motion due to wear in complex human body fluid environment, which may be termed as tribocorrosion. These degradations cause a local change in pH and ion concentration, causing premature failure of the implants due to its loosening and inflammations in the patient's body. Topographical modification of Ti6Al4V was reported to improve its mechanical and electrochemical properties and biocompatibility. In the present investigation, extensive studies have been undertaken to tailor the surface properties of Ti6Al4V for bio-implant application by surface topographical modification by (a) ultrafast laser surface structuring and (b) nanosecond laser surface structuring and near-surface microstructural modification and stress state modification by (c) laser shock peening.

Ultrafast laser surface structuring was conducted on Ti6Al4V using a Ti: Sapphire laser with a wavelength of 800 nm and pulse durations of 3 ps and 100 fs, varying peak fluence and scan speed. Laser surface processing leads to the formation of a periodically patterned surface with an average ablation depth of 37.25 µm - 42.13 µm and average surface roughness of 0.991 µm - 1.862 µm as compared to 0.169 µm average roughness of as-received Ti6Al4V. In the microstructure, there is the presence of fine periodic ripples with an average ripple width of 0.48 µm to 0.54 µm when processed with a 3 ps laser and the average ripple width of 0.17 µm in addition to the presence of very fine pits, deposited particles, and oxide dispersed surface

when processed with 100 fs laser. Surface structuring leads to defect-free periodic surface structures with grain refinement (subgrain size of 5.2 µm) as compared to as received Ti6Al4V (26 µm). There is a significant enhancement in nano hardness (5600-5800 MPa) and Young's modulus (139 – 148 GPa) as compared to as received Ti6Al4V ((nano hardness of 3800 MPa), (Young's modulus of 117 GPa)). The microhardness of the surface is improved (373 VHN - 395 VHN) as compared to 303 VHN of as-received Ti6Al4V. There is a significant improvement in the corrosion resistance in terms of a decrease in corrosion rate in the laser surface processed sample as compared to as-received Ti6Al4V in Hank's solution and also increase in pitting corrosion resistance in terms of increase in the critical potential for pit formation (E_{pit}) under a few employed parameters with both 3 ps laser (at a laser fluence of 0.063 J/cm^2 and a scan speed of 20 mm/sec) and 100 fs laser (at a laser fluence of 0.63 J/cm^2 and at a scan speed of 60 mm/sec). The tribocorrosion test showed a marginal decrease in the coefficient of friction in ultrafast laser surface structured samples, which increased with an increase in load as compared to as-received Ti6Al4V. A minimum coefficient of friction was observed for the samples processed with a 100-fs pulse width laser. The wear rate showed a significant decrease for both the samples processed with 100 fs and 3 ps laser pulse width as compared to as-received Ti6Al4V and increased with an increase in load. The synergistic behavior of chemical and mechanochemical interaction shows that there is reduced synergism behavior in ultrafast laser surface structured samples (1.62- 1.32 mm/year) as compared to as received one (3.5 mm/year).

Laser surface structuring (LSS) of Ti6Al4V was carried out using an Nd: YLF laser with a second harmonic wavelength of 527 nm and a pulse duration of 100 ns at varied laser fluence, scan speed, and line spacing. Nanosecond pulsed laser irradiation with overlapping resulted in the formation of linear continuous grooves on the surface due to ablation/evaporation of materials. There is the formation of oxides of titanium (TiO_2 and Ti_2O_3) whose mass fractions varied with process parameters. Due to LSS, there is increment in nano hardness (4.9 GPa - 6.3 GPa) and Young's modulus (140 GPa -153 GPa) when compared to as received Ti6Al4V (3.9 GPa, 123 GPa). The average microhardness of the laser-structured region was improved (393 VHN - 535 VHN) as compared to the as-received Ti6Al4V (303 VHN). The contact angle of simulated body fluid (SBF) against the structured surface (58°- 123°) showed increased contact angle as compared to as-received samples (50°). The laser surface structured samples (0.0028 – 0.00003137 mm/year) exhibited superior corrosion resistance as compared to the as-received Ti6Al4V (0.005156 mm/year). Laser surface structured sample with 141.5 J/cm^2 laser fluence, 50 µm line spacing, and 50 mm/sec scan speed offered maximum corrosion resistance (0.00003137 mm/year). The superior corrosion resistance of laser surface structured Ti6Al4V is due to formation of stable and compact passive layer. The tribocorrosion behavior in simulated body fluid against the ZrO_2 ball in fretting mode shows that due to laser surface structuring, the degradation rate was significantly reduced (5.3–67.2%) when compared to the as received one. With an increase in load, the coefficient of friction and material removal rate increases. The detailed calculation of individual components of degradation shows laser surface structured Ti6Al4V showed superior tribocorrosion resistance in terms of lower synergistic components (wear on corrosion and corrosion on wear) as compared to as received one

Finally, laser shock peening was performed using a Nd: YAG laser with a pulse duration of 10 ns, varying the power density from 2 GW/cm^2 to 8 GW/cm^2 and the pulse density from 178 pulses/cm^2 to 2132 pulses/cm^2. Detailed microstructural analysis reveals that laser shock peening causes microstructure refinement; the degree of refinement is higher for the samples with coating, and it increases with an increase in laser intensity and increase in pulse density. There is fragmentation of the β phase due to laser shock peening, which increases further with an increase in laser intensity and an increase in pulse density. There is increased microhardness (336 VHN to 487 VHN), nano hardness (4456 MPa to 7222 MPa), Young's modulus (121.3

GPa to 178.24 GPa) and introduction of compressive residual stress (-35.9 MPa to -385 MPa) in the laser shock peened samples compared to the tensile residual stresses in as-received Ti6Al4V (+133 MPa). The laser shock-peened samples exhibited enhanced corrosion resistance compared to the as-received material. Among the laser shock peened samples, the corrosion resistance has increased with an increase in laser intensity and pulse density. Laser shock peening results in increased tribocorrosion resistance in terms of reduced coefficient of friction, nobler open circuit potential during wear, and lower degradation rate than as-received Ti6Al4V. A detailed comparison of the above-mentioned results shows that the surface processing techniques applied on Ti6Al4V were predominantly aimed at modifying the surface topography (laser surface structuring using an ultrafast and short laser) and also modifying the stress state of the surface (laser shock peening). Eventually, all the surface treatments modified the microstructure (grain size, morphology and texture) and subsequently influenced the surface mechanical properties (microhardness, nanomechanical properties, wear resistance, tribocorrosion resistance) and electrochemical properties (corrosion resistance) of the samples. Though individual treatment was found to improve the surface mechanical and electrochemical properties when processed under optimum process parameters, however, a detailed comparative analysis shows that nanosecond laser surface structuring is most effective in reducing the overall degradation rate with superior bioactivity and cell viability.

Keywords: Ti-6Al-4V, Laser surface structuring, Laser shock peening, Nano-indentation, Tribocorrosion, Corrosion, Bioactivity, Wettability, Cell viability.