Enhancement of Wear and Corrosion Resistance of Beta Titanium Alloy by Laser Technology

Chi-Wai Chan[1], Seunghwan Lee[2], Graham Smith[3], Gianluca Sarri[4], Chi-Ho Ng[5, 6], Ahmed Sharba[4], Hau-Chung Man[6]

1 School of Mechanical and Aerospace Engineering, Queen's University Belfast, BT9 5AH, UK
2 Department of Mechanical Engineering, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark
3 Department of Natural Sciences, University of Chester, Thornton Science Park, Chester, CH2 4NU, UK
4 School of Mathematics and Physics, Queen's University Belfast, Belfast BT7 1NN, UK
5 Laser Engineering and Manufacturing Research Centre, Faculty of Science and Engineering, University of Chester, Thornton Science park, Chester CH1 4BJ, UK
6 Department of Industrial and Systems Engineering, Faculty of Engineering, The Hong Kong Polytechnic University, Hong Kong, China

Corresponding Author: c.w.chan@qub.ac.uk

Research Highlights

- Laser technology is a fast, clean and flexible method for surface hardening of TNZT.
- Laser can form a protective hard layer on TNZT surface without altering the surface roughness.
- The laser-formed layer is metallurgically bonded to the substrate.
- Laser-treated TNZT is highly resistant to corrosion and wear in Hank's solution.

Abstract

The relatively high elastic modulus coupled with the presence of toxic vanadium (V) in Ti6Al4V alloy has long been a concern in orthopaedic applications. To solve the problem, a variety of non-toxic and low modulus beta-titanium (beta-Ti) alloys have been developed. Among the beta-Ti alloy family, the quaternary Ti-Nb-Zr-Ta (TZNT) alloys have received the highest attention as a promising replacement for Ti6Al4V due to their lower elastic modulus and outstanding long term stability against corrosion in biological environments. However, the inferior wear resistance of TNZT is still a problem that must be resolved before commercialising in the orthopaedic market. In this work, a newly-developed laser surface treatment technique was employed to improve the surface properties of Ti-35.3Nb-7.3Zr-5.7Ta alloy. The surface microstructure and composition of the laser-treated TNZT surface were examined by grazing incidence x-ray diffraction (GI-XRD) and x-ray photoelectron spectroscopy (XPS). The wear and corrosion resistance were evaluated by pin-on-plate sliding test and anodic polarisation test in Hanks' solution. The experimental results were compared with the untreated (or base) TNZT material. The research findings showed that the laser surface treatment technique reported in this work can effectively improve the wear and corrosion resistance of TNZT. The enhancement of such surface properties was due to the formation of a smooth and hard layer on the substrate surface. The laser-formed layer was metallurgically bonded to the substrate, and had no concern of coating delamination or peel-off.

1. Introduction

Ti6Al4V alloys have long been considered as the workhorse in orthopaedic applications due to their excellent mechanical properties, corrosion resistance, and biocompatibility. However, their elastic modulus is still larger than that of human bone causing the problem of "stress-shielding" or osteopenia. The stress shielding effect which originates from the disparity of elastic modulus between implant materials and human bones causes a reduction in bone density and results in the loosening of implants in the long term [1]. Moreover, the presence of the toxic vanadium (V) element in the Ti6Al4V alloy also creates the concern of toxic ion release near the implanted area [2]. Recently, advances in materials technology have led to the development of beta-titanium (beta-Ti) alloys. Beta-

Ti alloys possess desirable properties over the conventional Ti6Al4V alloy, such as lower elastic modulus, super-elastic behaviours, and no concern of toxicity/allergy problems [3]. A variety of beta-Ti alloy systems constituted by different combinations of non-allergic/toxic beta-stabilising elements (Ti, Zr, Nb, Ta, Mo, Fe, etc.) have been developed. Among them, the quaternary Ti-Nb-Zr-Ta (TZNT) alloy has received the highest attention because of its lowest Young's modulus (around 60 GPa) and outstanding long term stability against corrosion in biological environments [4, 5, 6]. The alloying elements in TNZT, such as titanium (Ti), niobium (Nb), zirconium (Zr) and tantalum (Ta) exhibit excellent biocompatibility because they belong to the loose connection vascularized group with regards to tissue reaction [7]. Ti, Nb, Zr and Ta also have a considerably superior corrosion resistance due to the resultant surface oxides, such as TiO_2, Nb_2O_5, ZrO_2, and Ta_2O_5 [8].

Two practical considerations have to be taken into account when using the TNZT alloy in load-bearings in orthopaedic applications, particularly for the metallic femoral head, i.e. hemispherical ball joint. Firstly, the ball joint surface should be highly wear-resistant to minimise the formation of wear debris during the continuous dynamic movement between the socket and ball joint in real-life service. One way to achieve this is to increase the surface hardness. Secondly, the implant surface needs to be highly corrosion-resistant, as the surface comes in direct contact with different kinds of corrosive body fluids. More importantly, the crevice between the ball joint and the socket can be the weak point to initiate the corrosion attack. On account of this, proper surface treatment to form a very hard and corrosion resistant coating on the substrate can reduce the chance of implant failure due to corrosion attack or the combined effect of corrosion and wear. In the present investigation, we report on a novel laser surface treatment method to form a smooth and hard layer on the beta TNZT alloy. The wear and corrosion properties of the laser-treated surface were examined in detail and compared with those of the base TNZT material, showing significant improvement.

It is necessary to note that the TNZT alloy is a relatively new alloy system, and hence not much work has been done to investigate surface treatment to enhance the wear and corrosion properties. The existing studies in the literature can be split into three streams, namely (1) heat treatment to modify the microstructure and hence to improve the mechanical/functional properties [9, 10, 11, 12, 13], (2) laser 3D printing to control the structural architecture and composition [14, 15, 16, 17, 18] and (3) surface treatment to improve the bioactivity [18, 19, 20, 21, 22, 23, 24, 25, 26]. Few attempts on surface hardening of TNZT alloy, namely conventional gas nitriding in furnace, have been made in the literature [27, 28]. To the best of the authors' knowledge, the surface hardening of TNZT alloy by laser technology is believed to be one of the first attempts of its kind. Laser technology has the competitive advantages of short treatment time, non-contact, easy control of process parameters, clean and accurate in comparison with other surface technologies. Moreover, the laser can selectively treat at specific area with high precision and as there is a metallurgical bond between the treated layer and the substrate that there is no concern of delamination/peel off at the interface.

The state of the art of our proposed laser technique lies in the delicate control of some interrelated laser parameters, namely, laser power, material scanning speed, focus position and gas flow rate to form a smooth and uniform protective surface layer on the TNZT substrate. The laser power, scanning speed, and focus position can be considered as laser energy input to the substrate. If the laser energy input is too high, the surface will be melt out and the pre-manufactured precise surface finishing on the femoral head implant will be destroyed. On the contrary, if the laser energy input is too low, the surface layer will not be thick enough to serve as a barrier to protect the femoral head implant from corrosion, wear and a combination of both. The laser parameters used in experimentation were carefully chosen from a preliminary screening study [29].

2. Experimental Methods

2.1 Materials

The material was a 3 mm Ti-35.3Nb-7.3Zr-5.7Ta (TNZT) flat plate purchased from American Element, USA. It was cut into suitable size for experimentation. The chemical composition of the material is depicted in Table 1. Before the laser treatment process, the sample surface was ground and polished by a series of sandpapers following the standard procedure. Then the samples were cleaned and degreased ultrasonically in methanol for 10 min, rinsed in distilled water for another 10 min, and dried thoroughly in cold air stream.

2.2 Laser Surface Treatment

The laser surface treatment process was performed using a continuous wave (CW) fiber laser (SPI Lasers UK Ltd, UK). The TNZT surface was ground and polished by sandpapers down to 800 grit before the laser experimentation to ensure surface consistency. After cleaning with methanol and drying in air, the polished samples were irradiated with the fiber laser using the following processing parameters: laser power = 25W, laser scanning speed = 1 mm/s, focus position: 10 mm away from the nozzle tip, overlap neighbouring tracks was 0.3 mm (overlapping ratio of around 30 %) for constructing a uniform and defect-free surface layer. Pure nitrogen gas was delivered to the laser-irradiated area via the central and side jets at a flow rate of 30 L/min. The experimental setup is shown in the schematic diagram in Figure 1.

2.3 Surface Microstructure and Composition Characterization

The phases present in the treated and untreated surfaces were identified using X-ray diffraction (XRD, Bruker D8 advance) at 40 kV and 25 mA using Cu Kα radiation with a scanning rate of 1° min^{-1}. To avoid spurious signal coming from the substrate, grazing incidence X-Ray diffraction (GI-XRD) was used to characterise the microstructure of the thin laser-formed layer. GI-XRD was carried out with the diffraction angle varying between 20° and 80°, and an incident angle of 10^o to give the most recognizable pattern to determine the phase. The selection was based on a number of preliminary tests with different incident angles varying between 0.5° and 25°. The penetration depth of Cu Kα radiation in Ti is estimated at approximately 11 μm, and may be expected to be lower in the TZNT alloy due to the higher density, and so at 10^o incidence the information depth is less than approximately 2 μm.

X-ray photoelectron spectroscopy (XPS) was also performed to study the chemical compositions of the surfaces. Spectra were acquired using a bespoke ultra-high vacuum system fitted with a Specs GmbH Focus 500 monochromated Al Kα X-ray source, Specs GmbH Phoibos 150 mm mean radius hemispherical analyser with 9-channeltron detection, and a Specs GmbH FG20 charge neutralising electron gun. The survey and narrow scans were acquired over the binding energy range between 0 and 1100 eV using a pass energy of 50 eV and the high resolution scans were made over the C 1s and O 1s lines using a pass energy of 15 eV. Data processing and curve fitting were carried out using the CasaXPS software v2.3.16.

2.4 Wear Test

The coupling of ultra-high-molecular-weight polyethylene (UHMWPE) and Ti6Al4V represents the bearing pair challenged in orthopaedic implants, i.e. plastic acetabular cup against metallic femoral ball head [30]. Thus, the evaluation of the wear behaviour of TNZT against UHMWPE is an important criterion to determine the long-term performance and safety of the implants. In this study, a reciprocating wear test was employed to evaluate the wear properties of the laser-treated and untreated surfaces against UHMWPE. This was carried out by using a pin-on-plate sliding machine (TE99 Universal Wear Machine, Phoenix Tribology).

In the reciprocating wear test, an 8 mm diameter flat-ended UHMWPE pin was fixed in the sliding carriage. It was clamped and pressed endwise against the counter-face metallic plates, namely the laser-treated and untreated surfaces. A normal load of 50 N (or applied stress of 1 MPa) was chosen. The frequency was 1 Hz and the stroke length was 30 mm for test duration of 43200 cycles (about 2.5 km of sliding distance) in Hanks' solution (See Table 2 for the composition) at room temperature. The wear resistance was evaluated using the wear factor calculated by wear volume (mm^3) / load (N) x distance travelled (m). The wear factors for the laser-treated and untreated surfaces were determined, and the results were taken from the average of three repetitive tests. The wear marks left on the surfaces after the wear tests were captured by a 3D optical measurement system (Wyko NT8000, Veeco Instruments, Tucsan, AZ).

2.5 Corrosion Test

Anodic polarization tests were carried out to evaluate the corrosion properties of the laser-treated and untreated surfaces. The polarization tests were conforming to ASTM Standard G5-94 [31]. A potentiostat (EG & G Princeton Applied Research; model 273A, M352 software) with a standard three-electrode system was used. The test medium was Hanks' solution at 37 °C and with pH value 7.4. A pair of graphite rods was used as counter electrodes. The reference electrode was a saturated calomel electrode (SCE). A standard sample holder was used with the surface area exposed to the test medium controlled as 1 cm^2. The tests were started after an initial delay of 60 min in order to achieve an equilibrium state between the sample surface and test medium. The starting point was 200 mV below the open-circuit potential (OCP) and the scanning rate was 0.5 mV/s. The polarization tests were repeated three times for each sample to enable the reproducibility of test results.

3. Results and Discussions

3.1 Surface Microstructure (GI-XRD)

The microstructure of the laser-formed layer on TNZT surface cannot be straightforwardly characterised by classical theta-2 theta approach because the x-ray can penetrate through the thin layer and hit the substrate underneath. The resultant XRD pattern will be dominated by response from the substrate rather than the laser-formed layer which is of interest. The layer thickness was within the range of 500 nm to 1 um (see SEM micrograph in Figure 2). The GI-XRD patterns of the laser-treated and untreated surfaces at 10^o incidence angle are shown in Figure 3. As observed, the peak due to the (110) reflection at approximately 38.5^o diffraction angle clearly indicated the presence of bcc beta phase in both surfaces. The untreated TNZT surface (red line in Figure 3) exhibited only the bcc β phase, as shown by the presence of the (110) and (211) reflections. No alpha phase was detected. This is due to the presence of beta stabilizing elements (Nb, Zr and Nb) in the material which suppresses the formation of alpha phase.

In comparison, the XRD pattern of laser-treated TNZT surface (blue line in Figure 3) showed that the (110) peak intensity was significantly increased and a distinctive (200) peak at was found in the pattern. When carefully examining the region around the (110) peak (see the inset in Figure 3), a small (101) peak was found, indicating the presence of the alpha phase. The precipitation of alpha phase in the laser-formed layer is believed to be the major reason attributed for the enhancement of surface hardness observed in our previous study [29].

3.2 Wear Test (Pin-on-plate Sliding Test)

Figure 4 shows the wear factors obtained from the sliding contacts of UHMWPE pin against the laser-treated or untreated TNZT surfaces. In general, the wear factors are lower after the laser treatment for the overall tribosystem, and yet this trend is clearer for UHMWPE pins than TNZT plates. For the case of TNZT, the wear factor decreased by ca. 26% on average after the laser surface treatment, but the overlapped error bars appear to blur the improvement of the wear resistant properties by the laser treatment. Nevertheless, this is mainly due to the high level of scatter in the wear factor data of the untreated TNZT samples. Much smaller variations in the wear factors of the laser treated TNZT samples imply that the wear properties of TNZT became more stabilized and reproducible by the surface treatment. Moreover, wear grooves along the sliding tracks as revealed by the 3D profile images shown in Figure 5 are clearly visible only from the untreated TNZT plates after the wear tests, which support the improvement in the anti-wear properties of TNZT samples by the laser treatment. This can be ascribed to the formation of a hard oxide layer on top of the TNZT surface and consequent improvement in their mechanical properties [29].

For the case of UHMWPE, the reduction in the wear factors by the laser treatment (ca. 27% on average) is even more evident. This can be firstly linked to the improved wear resistant properties of the counter surface, namely TNZT, by the laser treatment, especially if three body abrasive wear was the dominant wear mode. Previous tribological studies of Ti-based alloys, such as Cp Ti [32] or Ti6Al4V [33, 34, 35], sliding against UHMWPE surfaces have also shown reduction in the wear volumes of UHMWPE, as a result of various surface treatments of Ti-based metallic materials, such as ion implantation [32, 33, 34, 35], thermal oxidation thermal oxidation [33, 35], or oxygen diffusion [33]. While detailed mechanisms are different for each case, a common factor related to the improved anti-wear properties in those studies is the formation of oxide layer and the improvement in water wettability of Ti-based materials [32, 33, 34, 35]. Consequently, improved water lubrication leads to the reduced friction and wear of the tribological interface, i.e. not only titanium metallic surface, but also UHMWPE. As reported in a previous study [29], improved water wettability of the laser-treated TNZT samples (static water contact angle from ca. 66 to 55°) is also evident as a result of oxide layers formed on the surface (see the section 3.4 for details) and is mainly responsible for the reduced wear factor of UHMWPE.

It is also interesting to note that the wear factors of UHMWPE are somewhat lower than those of TNZT for both untreated and treated samples (Figure 4). In view of abrasive wear mechanisms, this behaviour might be puzzling at a first glance as the hardness of TNZT is substantially higher than that of UHMWPE, and abrasive wear is expected to occur mainly on the softer side of the tribopair, i.e. UHMWPE in this study. Wear of titanium-based metallic materials in sliding against UHMWPE has, however, been reported in many earlier studies [32, 33, 34, 35], even though a direct quantitative comparison of the wear of UHMWPE vs metallic components is rare to date. One possible explanation is that initially generated wear debris from TNZT surface may be embedded on the softer UHMWPE side and act as abrasive grits against TNZT surfaces [33] as UHMWPE wear debris can hardly wear off TNZT surfaces. Due to low contact pressure applied in this study, ca. 1 MPa, adhesive wear is not considered as a major wear mode. Although the wear test was conducted in Hanks' solution which contains Cl- ions and can induce pitting attack to the metal surface, no pitting was found from both the laser-treated and untreated surfaces after wear tests. There were no signs of corrosive wear. Overall, the experimental results in the work are in agreement with the speculation made in the previous study [29] in that the increased surface hardness from the laser-formed hard layer is ultimately responsible for the improved wear resistance of the tribopair composed of TNZT and UHMWPE.

3.3 Corrosion Test (Anodic Polarisation Test)

The corrosion resistance of the laser-treated and untreated TNZT surfaces was evaluated by anodic polarization tests in Hank's solution at 37 ^{o}C, and the results are depicted by the polarization curves in Figure 6. The corrosion parameters extracted from the curves are shown in Table 3. It could be observed that the polarisation curve of the laser-treated surface obviously shifted to the left in Figure 6 and the curve also positioned higher than that of the untreated surface. This indicated that the laser-treated surface had a higher corrosion resistance given the higher open-circuit potential (OCP) and smaller current density values. The current density was at least one order of magnitude smaller than the untreated surface. The improved corrosion resistance of the laser-treated surface could be attributed to the presence of the inert and passive oxide film on the laser-formed layer. To verify this hypothesis, surface XPS analysis was carried out to characterise the chemical composition and structure of the oxide film. A comparison was made between the laser-treated and untreated TNZT surfaces. The results are shown and discussed below in section 3.4.

It is to note that no pitting was identified in both curves, and this observation reinforced the argument in the wear test section that corrosion wear was not a major mechanism contributed to the loss of materials for both laser-treated and untreated surfaces. Hanks' solution is a commonly used medium in corrosion tests for bio-implant materials [36]. The absence of pitting attack after testing in Hanks' solution showed that both the laser-treated and untreated TNZT surfaces exhibited excellent resistance to localised corrosion, and can be used in applications where pitting corrosion is a concern.

3.4 Surface Composition (XPS)

It is believed that the outstanding corrosion resistance measured in the polarisation tests was due to the formation of highly protective oxide film on the metal surface in an oxidizing medium, such as Hanks' solution. However, the surface oxide film is normally amorphous or of low crystallinity and is very thin, namely in range of a few nanometres, and hence it is very difficult to detect by techniques such as EDS and XRD. In this work, the surface-sensitive analytical technique of XPS was used to study the oxide film in order to build up a thorough understanding of the chemical composition and structure of the topmost surface layer. XPS survey and narrow scans were carried out on the laser-treated and untreated TNZT surfaces, and the scans were done at the outermost surface (without sputter cleaning), i.e. at 0 Å depth. The XPS survey scans showed that, apart from the presence of the expected key elements (Ti, Nb, Zr, Ta, and O), both laser-treated and untreated surfaces showed the presence of carbon (C) in the form of hydrocarbons at 29.3 at% and 37.8 at%, respectively. It is believed that carbon was present as a contamination from environment or cleaning process.

Figure 7(a-j) show the XPS spectra of different elements obtained from narrow scans over the Ti 2p, Nb 3d, Zr 3d, Ta 4f, and O 1s lines for the laser-treated and untreated TNZT samples. The curve fits to the data were made with line-shapes, doublet separations and doublet intensities constrained to known reference values for the chemical states indicated in the Figure. The Ti 2p XPS spectra of the untreated surface (Figure 7a) showed that while the outermost oxide layer contained mainly the TiO_2 (or Ti^{4+}), small amounts of sub-oxides (TiO or Ti^{2+}, Ti_2O_3 or Ti^{3+}) and some metallic Ti were also found. In comparison, the outermost oxide layer on the laser-treated surface (Figure 7b) was purely made up of TiO_2 and no other sub-oxides were detected in the oxide film. This indicates that heating by laser radiation is sufficiently effective to drive a complete oxidation of Ti into Ti^{4+} on the TNZT surface. Similar observations can be found from the spectra of other alloying elements: Nb 3d (Figure 7d), Zr 3d (Figure 7f), and Ta 4f (Figure 7h). A complete oxidation of these elements was found in the outermost oxide layer on the laser-treated surface, and no other sub-oxides were detected. In contrast, the Nb 3d, Zr 3d and Ta 4f spectra from the untreated surface showed incomplete oxidation with small amounts of sub-oxides present in the outermost layer. A summary of different oxides detected in the outmost oxide layers on the laser-treated and untreated surfaces is given in Table 4. The findings in the XPS analysis indicated that the corrosion resistance of TNZT originated from the spontaneous formation of TiO_2-based passive oxide on the surface. Further, a more protective oxide can be obtained by laser surface treatment due to complete oxidation of the alloying elements, particularly Ti into TiO_2 and Nb into Nb_2O_5. TiO_2 and Nb_2O_5 are well known for their extremely high corrosion resistance and thermodynamic stability [8].

4. Conclusions

In this study, the influence of laser surface treatment on the wear and corrosion resistance of beta Ti-Nb-Zr-Ta (TNZT) alloy was studied, and the results were compared with the untreated (or base) material. To understand the mechanisms to protect the TNZT from wear and corrosion in Hanks' solution, the surface microstructure and composition were characterised by grazing incidence x-ray diffraction (GI-XRD) and x-ray photoelectron spectroscopy (XPS). The following conclusions were reached:

1. After careful selection of the laser process parameters, a smooth and uniform hard layer was formed on the TNZT surface.
2. The GI-XRD results indicated that the laser-formed hard layer comprised mainly the beta phase with the precipitation of alpha phase in the microstructure.
3. The laser-treated surface showed an improved wear resistance in sliding against UHMWPE in Hanks' solution, as evidenced by the smaller amount of material loss for both TNZT and UHMWPE in the pin-on-plate sliding test.
4. The laser-treated surface also exhibited a better corrosion resistance in Hanks' solution at 37 ^oC. This can be evidenced by the higher open-circuit potential (OCP) and small current density values in the anodic polarisation test.
5. The XPS results showed that the outermost oxide layer on the laser-formed hard layer mainly consisted of TiO_2 and Nb_2O_5 which contributed to the outstanding corrosion resistance of the surface.

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