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Enhancing the Properties of Ti_6Al_4V as a Biomedical Material: A Review

V.E. Annamalai*, S. Kavitha and Sarah Ann Ramji

Department of Mechanical Engineering, SSN College of Engineering, Chennai 603110, India

Abstract: The alloy Ti_6Al_4V has evolved as a good biomedical material, by virtue of its bio-compatibility. In order to make implants out of this material, it has to be shaped and processed. Shaping this material by conventional manufacturing methods like machining, welding and brazing presents a huge challenge. This challenge has been met by various approaches like additive manufacturing, surface alloying and heat treatment. Additive manufacturing processes are used for shaping; coatings and surface alloying are used for property improvement; heat treatment is used for improving the machinability. The processing method has an impact on the final properties of the product. This review attempts to trace the development of methods and practices for converting Ti_6Al_4V into a useful material for biomedical applications.

Keywords: Biomaterial, biomaterial processing, biomaterial testing, property modification, Ti_6Al_4V.

1. INTRODUCTION

Biomedical advancements have lead to the creation of prosthetic limbs, joints, healing plates, stents and various other devices that help people with various ailments and handicaps. This has created a demand for biomaterials. Biomaterials, if they are to be used in the human body, must not react with tissue and preferably have a density that is less than the density of bone. Excessive corrosion will cause the implant to disintegrate. Additionally, biomaterials must possess mechanical properties like fatigue strength, wear resistance and good machinability as well as other beneficial properties. Such strict requirement of properties restricts the use of several materials for biomedical applications. Only a few materials pass these stringent requirements. Ti_6Al_4V alloy is one such material.

To be able to utilize a biomaterial, one has to know how to improve the properties like biocompatibiliy as well as know how to convert it to required size and shape. Hence, knowledge on various processing methods for 'in-use' property enhancement as well as knowledge on how to machine the material is important. The purpose of this review is to gather and describe developments in both these fields of machining and processing Ti_6Al_4V so that its value as a biomedical material is enhanced.

2. ASSESSMENT AND IMPROVEMENT OF BIO-COMPATIBILITY

One of the most attractive features of Ti_6Al_4V is its excellent biocompatibility. This permits the alloy to be one of the most widely used materials in biological implants, and other biomedical applications as well. Several studies have been carried out on how to improve the biocompatible properties to enhance its biological applications. To improve properties such as corrosion resistance and fatigue resistance to enable Ti_6Al_4V to be used as a biomaterial, studies on coatings and surface modifications have been carried out. By changing the properties of the surface, the alloy may be transformed into a more efficient biomaterial with less chance of failure. Calcium phosphate, hydroxyapatite, oxide film and various other coating materials have been proven successful [1].

2.1. Methods to Improve Cell Attachment

It is possible to improve properties of Ti_6Al_4V implants, in such a way that the healing time is reduced and the bone formation increases. Physical and chemical changes, including micron changes, are used to achieve these properties [2]. The conclusion of the study was that osteoblasts, when grown on Ti_6Al_4V surfaces, give better phenotypes, and the process of growing of these osteoblasts is moderated, in comparison with those grown on polyetheretherketone (PEEK). Also, implants made with Ti_6Al_4V can be modified to possess better mechanical properties by using electron beam melting [3]. Using human embryonic cells, or stem cells, mesodermal progenitors have been derived (hES-MPs-human embryonic stem cell-derived mesodermal progenitors), that can produce a large number of cells, which may be used in bone engineering and skeletal engineering applications. The cell attachment and growth behavior of Ti_6Al_4V scaffolds made by EBM (Electron Beam Melting) technique have been studied. This process of combining stem cells with metallic scaffolds supports the growth and attachment of cells, and thus has the potential for the next level of bioengineering.

2.2. Controlling Roughness of Surface

Roughness is one of the principal mechanical factors affecting the biologically inclined properties of Ti_6Al_4V. By creating a rough surface on Ti_6Al_4V implants, the surface area is improved, and hence the bond between the implant and the bone can be made to last longer. Barranco *et al.* [4]

*Address correspondence to this author at the Department of Mechanical Engineering, SSN College of Engineering, Chennai 603110, India;
Tel: 09144-27474844; Fax: 09144-27475063;
E-mail: annamalaive@ssn.edu.in

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studied the influence of the microstructure and topography on the barrier properties of oxide scales thermally generated at 700 °C for 1 h on Ti_6Al_4V surfaces after blasting with coarse Al_2O_3 particles and fine SiO_2 and ZrO_2 particles. Microstructure, blast properties and corrosion behavior were studied. A needle like oxide growth formation was observed on the fine blast piece, whereas, the piece obtained by coarse blasting showed a globular morphology. These morphological changes influence the corrosion response, when tested in Hank's solution. The globular morphology obtained from the coarse blasting resulted in properties indicating a longer bone-implant adhesion, and corrosion properties were improved as well. All existing studies on roughness consequences on the biocompatibility of Ti_6Al_4V are on the micrometric scale, since achieving nanometric roughness is a challenge. Roughness on a nanometric scale was created and its influence on various properties was tested and was found that the rougher the surface, the higher the wettability. The morphology also changed from spherical to a spindle like structure, when moving from smooth to rough surfaces. Within a certain range, adhesion strength was found to increase with surface roughness. Greater number of cells was formed on the smoother surface. Thus, to conclude, roughness on a nanometric scale has a widespread influence on several properties. Another study showed that, UV irradiation as well as the biometric surface roughness of Ti_6Al_4V ultimately affects the cell growth and grip. The conclusion of this study was that the wettability on the surface of Ti_6Al_4V is negatively correlated with UV irradiation time as well as surface roughness [5].

2.3. Surface Modification with Lasers

Ti_6Al_4V used in dental implants can be surface textured with fiber lasers [6]. This technique of surface modification of the alloy will naturally change its cytocompatibility. Pulses of different time intervals were used, and it was found that while nano second pulses gave high thermal effects, the other pulses (pico and femto seconds) showed minimal effects. Attachment of cells on these surfaces were also studied. It was concluded that on the surface of the implant, different parts could be made to either promote or reduce cell attachment, by changing the patterns used. This method of laser pulses is a lower cost method, and can be used in medical implants to modify the surfaces, and to change the properties as required. Thermal oxidation could be used to modify the surface of Ti_6Al_4V, which could be used for bio-implementation. When the process was carried out for a longer duration, thickness and crystalline nature observed were greater, in the layer, which was found to contain rutile and anatase. This treated sample showed a good apatite formation.

Surface modification of Ti_6Al_4V was carried out in an alkali medium and adhesion, morphology and bioactivity were tested. After chemical treatment was carried out in an alkali solution, in a mixture of NH_4F and H_3PO_4, anodic oxidation took place, followed by thermal treatment [7]. A bioactive layer resulted with the growth of calcium-phosphorous compounds. This bioactivity was not affected by thermal treatment, though from this, dehydration resulted. Another layer that resulted was a non bioactive nano tubular layer, which was activated by the thermal treatment.

2.4. Collagen Coating

Different biological reactions occur on the surface of Ti_6Al_4V substrates, and collagen coating is said to be one of the methods to change the reactions that occur. An easier way to coat this layer on Ti_6Al_4V was created [8]. The intermediate layer used was Ca-P and collagen was coated over it. Cell behavior and growth were naturally changed with the introduction of this pre-coat. Since this method produced a uniform coating, it can be applied in several medical and biological applications. Similar testing of cytocompatibility was also done, comparing the results of Ti_6Al_4V with two other alloys, $Ti_{45}Al_{8.5}Nb$, and Ti_6Al_7Nb. When corrosion was tested, it was found that potential and current density of corrosion were similar for all three alloys [9]. Further studies of the corrosion properties were performed in two solutions, artificial saliva and Ringer's solution [10]. Surfaces that were subjected to grinding did not have as good a corrosion resistance as a polished surface. Additionally, pitting occurred in the ground part, while testing in Ringer's solution.

2.5. Improving the Pull Out Strength

Ti_6Al_4V is also used to manufacture cortical bone screws, and these screws have a pull out strength value that varies with different methods of surface treatment oxidization. Four methods were tested, micro arc oxidization, in a plasma environment, with an anodisation unit and micro arc oxidization in a sodium hydroxide solution [11]. The result was the formation of a hydroxapatite layer, and for each method, pull out strength was tested. In another study, only the micro arc oxidization method, and then hydrothermal treatment was used to form hydroxyapatite layer on Ti_6Al_4V [12]. From the process, which was carried out in β-glycerophosphate and calcium acetate solution, phosphorous and calcium coated solution which contained titanium were obtained. After each process, wear tests were carried out in an environment of simulated body fluids. Hydroxyapatite layer was observed after the heat treatment had taken place, and this bio active layer was found to improve wear resistance and adhesion properties.

2.6. Inhibiting Bacterial Growth

Conditions that lead to the failure of the implants must be studied and overcome to improve implant life. Bacterial formation on the surface of implants is a potential hazard. Thus, studies were conducted to inhibit their formation on the surface of the titanium aluminium alloy, as well as to increase anatase formation and better response of osteoblasts to the surface [13]. It was discovered that the voltage applied for the treatment of the alloy affected the properties. For low voltages, less osteoblast formation and spreading were present, favorably, but, there was an increase in bacterial attachment compared to the higher voltages.

2.7. Preventing Degradation

Biological implants do have the tendency to degrade, and one of the governing factors is "stress dependent electrochemical dissolution" [14]. This study focused on hip implants especially, studying various factors like wear resistance, plane stress, chemical conditions, contact loads, and their influence on each other. The surface degradation was observed under these varying conditions. One of the outcomes discovered was that implant life was more affected by transverse micro motion (as opposed to longitudinal micro motion). Weight of the patient also affected life expectancy of the implants. To extend the longevity of the implant, joint fluid aeration, choosing a proper microstructure of the material as well as making sure the mating surfaces have proper tolerance values are some of the techniques that were proposed.

2.8. Mineralizing with Calcium Apatite

Since one of the main components of prosthetic limbs is Ti_6Al_4V, when there is not sufficient interaction between the bone and this alloy, the limb will fail. A solution to this problem is osteointegration. This can be achieved to an extent by mineralizing the surface with calcium apatite [15]. The final mineralized product was found to possess better retention of the human bone recombinent morphogenic protein-2, thus leading to ultimately stronger implants. It was observed that Ti_6Al_4V might not possess as good a biocompatibility value as a vanadium free alloy [16]. Biofilm formation and platelet addition was studied, and it was concluded that there was a higher level of thrombogenicity as well as cytotoxic properties in Ti_6Al_4V, compared to a non-vanadium alloy, Ti_6Al_7Nb.

2.9. Creation of Composites

The implementation of composites for altering the properties of the material has become a wide area of research nowadays. A study on laser processed TiN reinforced composite coatings was evaluated [17]. Using scanning electron microscope the micro structural analysis of the composites was evaluated and phase analysis was performed with X-ray diffraction. The tribological performance of the coatings were examined, in simulated body fluids, up to 1000 m sliding distance under 10 N normal load. The results show that the 40 wt.% TiN reinforced coatings exhibited the highest wear resistance. Further study on biocompatibility revealed that these coatings provided enhanced cell-material interactions and were non-toxic due to their high surface energy. The results reveal that they are best suited for wear resistant contact surfaces and load bearing implant applications.

Titanium-metal-matrix composites (Ti-MMC) like Ti_6Al_4V-SiC_f possess large specific resistance and can operate at temperature up to 800°C. Hot Isostatic Pressing (HIP), a reliable but expensive manufacturing method is used to produce these composites [18]. Centro Sviluppo Materiali SpA (CSM) has developed and patented an experimental plant for co-rolling at high temperature, sheets of titanium alloy and silicon carbide monofilament fabrics to cut the production costs. About 40% reduction of costs is achieved by the experimental Roll Diffusion Bonding (RDB) pilot plant. Comparing the results of both the process, the results show that the fibre-matrix interface is stable while RDB composite and has better mechanical properties. Another study on the micro chemistry and mechanical behavior of the composite produced by HIP was performed [19]. An extensive study to evaluate its capability to tolerate the in-service conditions of turbine blades working at middle temperatures in aeronautical engines was carried out. Another study on composites was boron additions on TiC/Ti_6Al_4V composites [20]. The results reveal that the compressive strength and hardness has increased.

3. LASER MELTING AND PROCESSING OF SURFACES

Laser melting is one of the several additive manufacturing processes that are being used today. With Ti_6Al_4V alloys, this method is also increasingly used. Selective Laser Melting involves usually a laser beam with high power as an energy source, and digital information in the form of 3D CAD data as input information.

3.1. Selective Laser Melting

Better mechanical properties can be achieved by Selective Laser Melting process. Song *et al.* [21] used selective laser melting (SLM) to manufacture different Ti_6Al_4V parts, and proposed a processing map pertaining to three melting mechanisms. They created a smooth surface and high micro hardness part, under certain conditions (110 W power, 0.4 m/s scan rate). By following a continuous melting mechanism, they discovered that the density of the part they obtained was close to the value of bulk Ti_6Al_4V.

3.2. Impact of Operating Temperatures

As a continuation of the research mentioned above, further studies were conducted on methods to improve mechanical properties. It was found that operating temperatures have a great influence on various qualities of the selective laser melting, especially the density levels. Since these temperatures directly depend on process parameters, it was investigated whether, without post processing, denser parts may be created [22]. Lower porosity and higher density parts were created, under the same laser conditions (110 W. 0.2 m/s) The results showed that number of pores and distinctness of the layers were directly proportional to the scan speed. Also, varied microhardness values were obtained, since porosity and α phase increased.

Studies were performed to optimize the control of production of porous Ti_6Al_4V parts, using SLM, since variations occurred in the designed and final products [23]. With the aid of a micro CT based protocol, the mismatch diminished to 5% from 45% in the pore size. This was done by integrating the mismatch between the two in a second run. This can be applied to various other parameters as well, like surface area, strut thickness, porosity. It was concluded from this study that “increased morphological controllability increases mechanical controllability”.

3.3. Torsional Loading Tests

Porosity increases with scan speed and porous structures are inherently brittle. Several studies have been conducted on improvement of the properties of porous structures. Torsional loading tests were performed on samples of this alloy created by laser processing [24]. Each sample had varying porosity levels, 0%, 10%, 20% and the deformation was studied, with the view of understanding the mechanical properties involved. The study showed that the strength as well as modulus reduced with an elevation in porosity levels. Furthermore, it was observed that ductile deformation and strain hardening was present. This led to the suggestion that, using laser processing, the brittleness in porous materials could be mitigated, which implies a possible usage in metal implant applications, especially those that bear loads. Thus, improvement of the porous properties of Ti_6Al_4V alloys has been achieved to an extent.

3.4. Impact of Cryogenic Environment

Contemplations arouse whether new structural components would arise by surface melting of Ti_6Al_4V alloy. Tests were carried out using CO_2 laser, varying the power and scan speed [25]. Zielińskia *et al.* [26] created a cryogenic environment by dipping in a liquid nitrogen bath. They discovered, on measuring Vickers hardness of different sections, that a 1.5 mm thick transformed surface layer had constituents that deviated from those of the base metal. The layer had a greater micro hardness value and different layers were identified. This method, they stated, could be used to elevate the surface properties, which would have implications in the biological field. One drawback was the formation of surface cracks, which needed to be overcome. In 2012, they described a new laser treatment method, keeping the cryogenic conditions. The remelting was performed using continuous CO_2 work laser (between 3 and 6 kW, scan speed 0.5-1 m/s).

The purpose was to use the treatment for biological applications, specifically for implants, which need to be present in a biologically corrosive environment. Tests were performed in Ringer's solution, and it was concluded that the tribological characteristics were improved, inspite of the presence of surface cracks. Further potential areas of research could involve a method to completely eliminate the surface cracks that occur with cryogenic laser melting.

3.5. Plasma Arc Oxidation

Other research conducted in the area of laser processing involved a study of plasma arc oxidization with EIS (electrochemical impedance spectroscopy) [27]. Keeping current density constant, it was observed that with change in voltage, coating structure was modified. A study of the charging process that occurred across the breakdown voltage was performed.

Laser melting is a popularly used additive manufacturing process for machining Ti_6Al_4V alloys. Mechanical properties of the final product have been improved by several methods, and the brittleness of the porous structures was reduced.

4. COATINGS

Coatings are one of the recent techniques that are implemented in the process of improving the properties of the titanium aluminium alloys. The components made up of titanium aluminium alloys are subjected to various effects like mechanical and electrochemical effects. Arslan *et al.* have investigated the tribocorrosion behavior of Ti_6Al_4V alloy [28]. The science of surface alterations resulting from the interaction of mechanical loading and chemical reactions that occur between elements of a tribosystem exposed to corrosive environments is described as tribocorrosion.

4.1. Diamond Like Coatings

DLC (Diamond like carbon) coating is applied by using closed field unbalance magnetron sputtering (CFUBMS). Tribocorrosion experiments were performed in a pin-on-disc tribotester under electrochemical polarisation in NaCl 1 wt.% solution. The structural analysis of the coatings performed using Raman spectroscopy and scanning electron microscopy (SEM) shows that the coating protects the alloy and results in good performance under corrosion and tribocorrosion conditions.

Another method of coating was carried out by Chen *et al.* [29]. By using DBD (Dielectric Barrier Discharge) plasma gun at low temperature (<623 K), with methane as a precursor and argon as dilution gas at atmospheric pressure, DLC thin films had been deposited atop the Ti_6Al_4V alloy. Structural analysis was performed using Laser Raman spectroscope and X-ray photoelectron spectroscopy. Analysis on surface morphology and adhesion between coatings were also investigated. The results show that it is feasible to prepare a DLC thin film of 1.0 μm thickness by plasma gun possessing surface roughness about 13.23 nm R_a. It also has good adhesion properties and friction and wear-resistant behaviors. A study was performed by Nibennanoune *et al.* [30] on DLC deposited alloys to evaluate residual stresses using micro-Raman spectroscopy. AFM analysis was also performed to determine surface roughness. It was observed that the DLC coating has reduced the residual stress intensity to about half the value compared to the substrates without DLC. Though the seeding process has enabled the generation of smaller grains and led to better surface finish, it also has a partial opposite effect on stress intensities.

A duplex treatment to obtain a GLC (Graphite like carbon) coating was studied which involves nitrogen ion pre-implantation as well as the technique of gradient interfacial transition [31]. A systematic investigation was carried on arsenic deposited coating systems by Raman spectrometry, scanning electron microscopy, nano-indentation, atomic force microscopy and scratch tests. The friction as well as wear performance in two varying water environments (sea and distilled) was evaluated by a ball-on-disk tribometer. The results revealed that it possess greater hardness and adhesion strength. It also shows great improvement in tribological factors and demonstrated best friction and wear behaviors.

4.2. Molybdenised Coatings

By using the technique of "double-glow plasma surface alloying (DPSA)", properties like wear resistance and lubricating effect at high temperature were achieved. Lubricating property was attributed to the formation of molybdenized layer on Ti_6Al_4V [32]. This layer was composed of Mo-deposited layer and Mo-diffusing layer. This technique also improved surface hardness considerably. Another study using the above technique to improve surface hardness and impact resistance was performed using Cr-Mo layers [33]. The deposited layer contains $Cr_{1.93}Ti_{1.07}$, Cr_2Ti, FeCrMo, and $Cr_2Ti_4O_{11}$ compounds. Cu/Mo compounds were introduced as interfacial modification layers to experiment their effect on the interfacial microstructure and the mechanical properties of SiC_f/Ti_6Al_4V composite. The study reveals that the copper coating has completely diffused into the matrix and formed brittle structures such as a Widmanstaten structure which contained Ti_2Cu and α-Ti resulting in Mo-Ti mixed coating. The longitudinal tensile strength of the composite is outstanding as the coating can inhibit the fiber/matrix interfacial reaction.

4.3. Ultra-High Molecular Weight Polyethylene (UHMWPE) Coating

Another type of coating studied was a thin film of Ultra-high molecular weight polyethylene (UHMWPE) on Ti_6Al_4V using dip coating method [34]. Tribological performance of this coating (thickness of 19.6 ± 2.0 µm) was analysed using 4 mm diameter Si_3N_4 ball counterface in a ball-on-disk tribometer for different normal loads and rotational speeds of disk. The results reveal that it exhibits high hydrophobicity with water (contact angle of 135.5±3.3°) and meets the requirements of cytotoxicity test using the ISO 10993-5 elution method. Implementation of different aluminium coatings was also studied on commercial Ti_6Al_4V titanium alloy to enhance its high temperature corrosion resistance by metal-organic chemical vapor deposition from aluminum tri-isopropoxide [35]. The mechanical and adhesion properties to substrates were evaluated by indentation, scratch and micro tensile tests. Hardness and rigidity of the films increase with increasing deposition temperature. The hardness of the coatings prepared at 350 °C and 480 °C is 5.8 ± 0.7 GPa and 10.8 ± 0.8 GPa respectively and their Young's modulus is 92 ± 8 GPa (350 °C) and 155 ± 6 GPa (480 °C). Scratch tests cause adhesive and cohesive failures of films grown at under specific temperatures.

4.4. Intermetallic Matrix Composite Coatings

A coating of intermetallic composites on Ti_6Al_4V alloy was also studied by developing an *in situ* method to synthesize the TiN reinforced Ti_3Al intermetallic matrix composite (IMC) coatings on the alloy. This method involves two steps, namely, depositing pure Al coating on Ti_6Al_4V substrate by using plasma spraying, and laser nitriding of Al coating in nitrogen atmosphere. Study of the microstructure and mechanical properties of the coatings revealed that crack- and pore-free IMC coatings can be made through this method. The mechanical properties of coatings and the morphologies of TiN dendrites were strongly dependent on laser scanning speeds (LSS) used in nitriding. Deposition of multi-layered $Ti_{50}Al_{50}N/Ti_{70}Al_{30}N$ and mono-layered $Ti_{60}Al_{30}Si_{10}N$ on the alloy has been found to provide effective protection to the substrate alloy and improve the cyclic oxidation resistance [36]. The effect of nitrogen pressure content was also investigated on the composition, structure and mechanical/tribological properties of arc ion plating (AIP) CrN coatings [37]. As the nitrogen pressure increased the main phases changed from CrN + Cr2N + Cr to CrN. The transformation of texture of CrN was observed to be CrN (220)-oriented from CrN (111)-oriented. The results revealed that CrN coating acts as a good wear resistance layer for Ti_6Al_4V substrate. Properties like cavitation erosion (CE) and water droplet erosion were also investigated through the study by Mann *et al.* [38]. In this study, coating of commercially available SHS 7170-cored wire was obtained on Ti_6Al_4V alloy by Twin wire arc-spray (TWAS) and then subjected to surface treatment with high-power diode laser (HPDL). The CE resistance of the SHS 7170 (TWAS-coated) samples after HPDL treatment had improved greatly, evaluated as per ASTM G-32-2003. This improvement is due to the elimination of pores, reduction of hardness and brittleness and increase in fracture toughness. The results were similar to the water droplet erosion resistance.

4.5. Hydroxyapatite Coatings

There are numerous studies on hydroxyapatite and magnesium apatite formation on the alloy substrate to improve properties like bone formation, antibacterial activity etc. Yang *et al.* [39] have done a study on coatings containing calcium and phosphorous which induce bioapatite quickly. This coating was fabricated by Plasma Electrolytic Oxidation and studied using SEM and 3D profile. The ceramic coating exhibits a rough porous morphology and the chemical phases are anatase and rutile TiO_2, with calcium-phosphorus ratios of the two samples being above 1.67. In another study, bi-functional coatings of the calcium deficient carbonated hydroxyapatite (CDHA) were developed on titanium alloys by using a biomimetic coating process. An approved bisphosphonate drug, alendonate sodium (AS) which is used for the treatment of osteoporosis was loaded into the inner layers of CDHA coatings [40].

The experimental results revealed that the co-precipitation method had greater benefits in terms of optimum AS content in local area, which is beneficial for osteoblast cells proliferation. It is also expected that the co-precipitation approach has potential for bone tissue engineering applications. Study on magnesium apatite coatings were also incorporated which is according to $(Ca_{10}\text{-}xMgx)(PO_4)_6(OH)_2$, where x = 0 to 2, which was formed through a sol-gel dip-coating method [41]. The roughnesses of the magnesium coatings were directly proportional to the content of magnesium into the coatings and showed an opposite effect on hardness and young's modulus of coating. To vary the biological interactions taking place in Ti_6Al_4V substrate, collagen coating is considered to be an effective way. Preparation of uniform collagen coating is difficult by direct collagen coating method [8]. A study on simple and efficient method of coating was studied with a precoating of biomimetic Ca-P intermediate layer. Results also reveal that the cell proliferation of Collagen/Ca-P was significantly higher than those of the other specimen. Another study on various types of chemical pretreatment with NaOH, HF, or H_2O_2 to form bioactive hydroxyapatite (HA) coatings by a thermal substrate method has been reported [42]. This method has proved suitable for a rapid formation of uniform coatings on titanium and Ti_6Al_4V substrates at low temperatures, having chemical composition and film thickness under control. The major components of bone are hydroxyapatite and type I collagen. Analysis on generation of bone-like apatite coating on Ti_6Al_4V spinal fusion devices were studied using the two important methods: Sand-blasting treatment and chemically biomimetic growth. After these two treatments, bone like apatite was formed on the device. This is an important method to improve the interface adhesion strength and formation of osteoconductive coatings for implants [43]. Experimental results reveal that this method was favorable for the apatite coating.

Study on mechanical properties of the Hydroxyapatite (HA) coatings were done by Singh *et al.* [44]. Properties like fretting fatigue, toughness and abrasive wear resistance can be improved by incorporation of secondary ceramic and metallic reinforcements in HA. Results reveal that superior corrosion resistance is exhibited and tensile strength was improved significantly [44]. A slight improvement micro hardness and surface roughness was observed with reinforcement. Study on improving the antimicrobial activity with the help of micro arc oxidation process has given favorable results [45]. A micro porous oxide layer was formed on a Ti_6Al_4V alloy by this process in an electrolyte containing $(CH_3COO)_2CaH_2O$ + Na_3PO_4 with appropriate amount of silver containing agent. A wide spectrum antibiotic was also applied to the surface. Antimicrobial activity tests were conducted with JIS Z 2801 standard against *E. coli*.

5. SURFACE ALLOYING

Double glow plasma method of surface alloying was carried out on Ti_6Al_4V with W-Mo-N and W-Mo layers [46]. Using several analysis methods like employing a scanning electron microscope and using glow discharge optical emission spectroscopy and X-ray diffraction, chemical composition and morphology were studied. Also, other techniques were employed to measure the hardness and wear resistance (micro hardness testers and ball-on-disk wear testers). The surface modified layers were found to change in phase and composition along the depth, and in these layers, a microhardness gradient was detected. The surface layers were found to be almost four times harder than that of the actual Ti_6Al_4V substrate. The corrosion resistance and wear were definitely improved by these layers. In addition, it was discovered that since NaCl has a good lubricating effect, wear resistance in this medium was better than that in ambient air.

Another test using the same double glow discharge plasma technique was done by using Cr-Mo to modify the surface [33]. Using the Knoop hardness test, impact resistance and surface hardness were tested. The results showed that the deposited coating caused the surface hardness to increase. But, after the impact test, peeling of the modified layers was found, since the intermetallic compounds that resulted caused brittleness. Thus, it could be concluded that although better hardness and wear resistant properties resulted from this surface modification, a negative impact on the impact resistance properties was also present.

Tribological studies of alloyed Ti_6Al_4V surfaces were also carried out. Borided Ti_6Al_4V 's tribological performance against ceramic counterfaces in water were studied. It was discovered that among the two counterfaces used, the Al_2O_3 ball had more destructive force than the Si_3N_4 ball [47]. Also, using plasma surface alloying technique, a nickel modified layer on the surface of the alloy was created [48]. Various factors like microstructure, surface morphology as well as tribological behavior were studied. It was discovered that the roughness as well as hardness was elevated. The components present in the new layer are Ti_2Ni, TiNi and Ti phases, and the presence of Ti_2Ni was said to induce better tribological properties. Micro abrasion wearing was also discovered in the layer modified with Ni.

6. IMPROVING THE MACHINABILITY

Similar to surface alloying, various surface modification techniques have been employed with Ti_6Al_4V. The view is that by altering the nature of the surface, to some extent, the properties and ease of machining of the alloy may be improved.

6.1. Grit Blasting

One of the ways in which the surface of Ti_6Al_4V can be modified is by grit blasting [49]. It was found that the coarser the SiC grit, the rougher the resulting surface. When Al_2O_3 grit was used, the embedment increased, thus bond strength was lessened. Ti_6Al_4V was found to have the least grit embedment, compared to the other materials tested, stainless steel and bronze.

Hydroxyapatite coating and anodization was used to modify the surface to Ti_6Al_4V and their properties were compared to study adhesion characteristics. Various physical properties were studied. The best protein adhesion characteristics were found with hydroxyapatite coatings, and similar properties were obtained with high degree anodized Ti coats. These results are applicable in choosing orthopedic implant materials.

Surface modification by ion implantation is another potential method of changing the surface properties [50]. The surface properties can be increased by plasma surface treatments. Nitrogen plasma immersion technique of ion implantation was used to treat Ti_6Al_4V samples. Corrosion behavior and microstructure were used to test pure samples as well as samples which were modified. The layers were found to be resistant to corrosion attacks when treated by this method, and a reduction in passive current density was also observed. The layers formed were TiN and Ti_2N as well as nitrogen in a solid solution. These caused a very good polarization resistance value when impedance spectroscopy tests were performed. All these augmented properties are because of the continuous nitride layer that results. This layer slows down the chloride ions potential to enter into the substrate.

A second ion implantation technique is plasma based ion implantation (PBII). Nitrogen PBII was carried out in a stable heating source (200-1000^{o}C) [51]. Calcium oxide, strontium and barium cathode were used to produce electrons, that help with nitrogen ionization and sample heating. The thickness of the layer was found to increase, which was attributed to the thermal diffusion of nitrogen. The parameters were retested varying pulse and duration, but keeping temperature constant. It was concluded that by using high temperature PBII, tribological properties, mechanical properties as well as corrosion resistant properties were enhanced.

Using PBII, a nitrogen-oxygen mixture was implanted on Ti_6Al_4V at various voltage levels [52]. Hardness, chemical composition changes and structure were studied. In the layer, with an increase in the implant voltage, there was an increase with the wear resistance and the hardness. It was also found that the sample implanted with O_2 did not have as good properties as the sample implanted with N_2-O_2. Moreover, when the sample was treated with N_2-O_2 at -50kV, the wear rate was eight times lower than the untreated sample. Also, with implanted voltage, ploughing wear mechanism occurs, rather than the originally existing abrasive-dominated mechanism.

More nitrogen ion implantation into Ti_6Al_4V surface was done, mainly to study corrosion resistance, as well as surface roughness and morphology [53]. Atomic force microscopy and X-ray diffraction were used to study the properties. The optimum corrosion resistance was found to be occurring at an implantation fluence value of 2×10^{18} ions/cm^2. The microstruture variations were said to cause a corresponding change in corrosion resistance.

Using Laser Gas Nitriding, the corrosion and wear resistant properties of Ti_6Al_4V have been improved [54]. Using Nd-Yag laser in a nitrogen environment, a crack free surface was obtained and the properties tested. The results showed that the wear and corrosion resistance was enriched, and, in general, better properties were obtained by the Laser Gas Nitriding process.

Using various techniques and substances to modify the surface of Ti_6Al_4V, it is shown that various properties like surface hardness, roughness, wear resistance, etc can be modified. Nitrogen ion implantation appears to be the most popular recent trend in surface modification of this alloy, which creates good final surface properties.

7. IMPROVING THE MECHANICAL PROPERTIES BY HEAT TREATMENT

Heat treatment is a common method to improve mechanical properties of several metals. By heating the sample under consideration to a temperature above melting point and then cooling in an appropriate medium, the residual stresses that are present after machining can be eliminated. Heat treatment techniques can be applied to Ti_6Al_4V also.

7.1. Heat Treatment Studies on Titanium Alloy

Ti_6Al_4V reinforced with titanium boride was heat treated, and the percentage of β phase that had been transformed present in the matrix was found to be greater at higher quenching temperatures. This improves the strength at elevated and ambient temperatures, thus making it suitable for high temperature applications. But, when the aging temperatures increased, strength of the composite was lowered, since the size of the $\alpha + \beta$ phases and the amount present was raised. Excellent heat treatment properties after quenching and aging have been obtained under testing below 600^{o}C. Oxidation resistant intermetallic compounds can also be created by heat treatment, as already mentioned. Also, the Laser Gas Nitriding technique mentioned previously, which is also a heat treatment process that takes place in a nitrogen atmosphere, was seen to create an alloy of improved wear and corrosion resistance [54].

After heat treating, the micro morphology of Ti_6Al_4V forgings were modeled by using spatial tessellations feasible for FEM analyses of microstructure residual stresses [55]. The Johnson-Mehl tessellation was used, created by generalizing the Voronoi standard tessellation. Isotropic growth of the cells occurred, due to Poisson point process, resulting in nucleation site formation. The micro structure of Ti_6Al_4V was hence modeled and the residual stresses were studied. Ti_6Al_4V was mill-annealed in a vacuum furnace after investment casting process using zirconia stabilized with yttria [56]. The mechanical properties were discovered to be better than the alloy without heat treatment, and the time and temperature at which the process was carried out were determined to be the influencing parameters.

7.2. Understanding the Phase Transformations

Studies were made on the phase transformation that occurs in Ti_6Al_4V alloys during cooling. Diphase Ti_6Al_4V was cooled continuously from the α+β phase. A β to α diffusional transformation occurred throughout the cooling range. Changes in the α phase morphology were observed. Lamellar and granular structures were obtained, each at different cooling rates. Dąbrowski [57] concluded that the dilatometric effects that were noticed collaborated the phase transformation in Ti_6Al_4V. He also studied the effects observed when cooling of the α-β Ti_6Al_4V took place from the β phase. When cooling at a rate above the critical rate, β to α' martensitic transformation was found. Diffusional α to β transformation was further observed at a rate below the critical rate. Similar changes in the α phase morphology were again observed.

8. SHAPING BY JOINING

8.1. Welding Techniques and Studies

Joining and welding of titanium aluminium alloys has seen great advancements. Various welding and brazing techniques are used with this alloy.

8.1.1. Laser Welding

Laser welding and laser hybrid arc welding, have found great application in the machining of Ti_6Al_4V and several studies have been carried out on the weld parameters and final outcome.

A test performed with laser welding on this alloy was to study the effect on the weld beam by changing the focus position [58]. A Yb: YAG thin disk laser was selected, and 3 mm thick sheets were chosen to perform the bead on plate tests. Keeping welding speed and power constant, nine focus points were selected. Hardness, microstructure, defects and geometry were studied and compared with the view of selecting optimum focus position for butt welds. The conclusion was that "the best value of defocusing was -4 mm" since less undercut and penetrated area, and heightened penetration, as well as reduced grain size were observed in this setup. Further studies on the mechanical properties of these welds revealed that, in the heat affected zone, there was a variation in microstructure observed [59]. In the heat affected zone, as well as the fusion zone, martensite was discovered, and thus the strengthening in these zones was attributed to this discovery.

Serroni *et al.* [60] created butt joints using Nd-YAG laser in a Ti_6Al_4V grade 5 samples. They used two inert gases to create a non reactive atmosphere, and the power and weld speed were varied. Mechanical properties and corrosion resistance were studied. A lack of penetration of macroscopic defect was observed with low weld speed and high power. When fatigue tests were performed, defects such as undercutting were noticed, and fatigue strength thus was lowered. Using electrochemical micro cell technique, corrosion resistance was observed. The conclusion was that "joints with the best mechanical properties exhibit the best electrochemical properties" and "the weld bead shows a cathodic behavior with respect to the parent material".

One of the defects found was distortion, which was especially prevalent in thin plate welding. FEA models were selected for fibre thin plate welding of Ti_6Al_4V alloys of 0.7 mm thickness [61], and the distortion was studied using tensile tests. The plates were welded together with the help of continuous wave fibre lasers, and the tests performed. Successful thin plate welding was achieved for plates of the above mentioned thickness using Nd-YAG lasers [62]. To overcome the distortion that occurs, a fast, high powered and highly focused beam must be used. In Ti_6Al_4V alloy, the complexity of the microstructures affects the properties of the welds. Without heat treatment, the structure is predominantly α-martensite, which is characterized by not very high strength and low ductility. Heat treatment (to 950^{o}C) and then cooling in a furnace, led to the formation of a Widmastatten structure with an even balance of ductility and strength. Several studies have been made on the problem of distortion as well as residual stresses which occur in Ti_6Al_4V.

A detailed study on the residual stresses, both in laser welding and hybrid laser/MIG welding was conducted [63]. Using primarily electrical strain gauges to assess the residual stresses, the magnitude and location of these stresses were determined and residual curves were plotted. Various experimental data were presented, and this data can be used to make future upgrades to the existing process parameters.

8.1.2. Laser-Arc Hybrid Welding

Laser-arc hybrid welding is one of the weld techniques which may be used to machine these Titanium-Aluminium alloys. Statistical methods were used to optimize the parameters for this type of butt welding, with Ti_6Al_4V of sheet thickness 3 mm [64]. The effects of pulse frequency, beam power and various arc parameters were measured, and the microstructure was analyzed. Another test was conducted wherein butt joints of the same thickness were made with laser-arc hybrid welding and with laser welding minus a filler material [65] and their Vickers hardness was measured. Gap between the sheets in the former method were analyzed, and the effect of gap sizes on weld joints using CO_2-MIG hybrid laser was studied. With an optical deformation measurement system, joint deformation behavior has been studied.

It was discovered that welding steel with titanium alloys resulted in a weakness, due to the formation of intermetallic components. A study was performed on the welding of Ti_6Al_4V with steel (AISI 316L). This was done with electron beam and pulsed M-Day laser, through a pure copper interlayer [66]. The intermetallic phases formed were studied using different techniques, and a possible explanation was provided as to the way mechanical properties were determined by local phase content. The conclusion revealed that, although brittle phases could not be removed completely, a certain level of reduction was obtained by insertion of a copper interlayer (500 micrometers), and this brittleness affected the tensile stress values. Joining was made possible since the accumulation of the copper titanium and ferrous based layers locally had a less harmful effect on the weld strength. The small lifetime of the weld resulted in a thinner brittle layer, which the ductility of copper compensated for.

8.1.3. Combustion Synthesis Welding

Combustion synthesis method of welding was successfully carried out with Ti_6Al_4V and Al-C-Ti powders [67]. Compression of the powders was carried out in titanium aluminium pipes and the influence of aluminium powders and the reaction mode used on the welded joints were studied. Also, laser induced combustion synthesis (LCS) welding was conducted and the microstructure and mechanical properties were investigated. It was concluded that good mechanical properties in the weld seam were obtained using LCS welding. In the joint layer, nano sized TiC particles were discovered.

8.1.4. Linear Friction Welding (LFW)

Other than laser welding techniques, linear friction welding, (LFW) which involves a fixed and a moving chuck for holding the work piece, is also used. Finite Element Analysis software was employed to study the LFW in Ti_6Al_4V samples. A numerical simulation was carried out to study the stress and temperature fields, as well as phase transformation (metallo-thermo-mechanical theory was employed in part) [68]. The experiment was verified, and it was concluded that experimental and simulation results matched. This justified the use of numerical simulation methods [69].

8.1.5. Tungsten Arc Welding

Since many Ti_6Al_4V samples are created using additive manufacturing, the influence of the parameters of Tungsten arc welding on these samples was studied [70]. B grain size refinement was found to be virtually unchanged on the variation of pulse frequency and peak to base current ratio, but it changes with wire feed rate. Heterogeneous nucleation sites were created by the extra wire, and the columnar growth was changed to equiaxial growth due to the negative temperature gradient that arises in front of the liquidus.

8.1.6. Argon Arc Welding

Fatigue properties of various welds were studied using argon arc welding in a corrosive environment [71]. Salt fog and atmosphere, naturally corrosive environments, were employed in the study. One of the factors that affected fatigue life was weld seam holes. Also, while studying the influence of salt fog, it was determined that under high stress condition, the fatigue life does not reduce.

8.1.7. Ultrasoinc Welding

Ultrasonic welding on two dissimilar metals Ti_6Al_4V and an aluminium sheet (A6061) was successfully carried out [72] and the effect of the weld parameters on the micro structure, and also the mechanical properties, hardness, etc. were deliberated. The hardness was found to be elevated in both the matrices, and diffusion was discovered across the welding borders. By changing weld parameters and investigating, the strength of the joint was found to be optimum at welding time 170 ms and welding pressure 400 kPa.

8.2. Brazing

Several brazing techniques have also been used to join parts of Ti_6Al_4V.

Ultrasonic brazing using zinc filler material was done with dissimilar materials Ti_6Al_4V and Al_4Cu_1Mg in the absence and presence of silicon [73]. To regulate the formation of intermetallic compounds, pretreatment by hot dip aluminizing and as well as ultrasonic dipping was carried out, the latter being done in a molten filler bath. $TiAl_3$ was found in the aluminized coating and Ti_6Al_4V interface. When no silicon was used, there was no change in the interfacial area, but when silicon was used, $Ti_7Al_5Si_{12}$ was formed instead of $TiAl_3$ at the interface, due to the ultrasonic wave. The diffusion rate of Si was accelerated by ultrasonic wave in the molten filler material at temperature of 420^{o}C. This change in compound form resulted in a corresponding change in morphology, to a lamellar structure from a block structure. Maximum shear stress visible was 138 MPa in the $TiAl_3$ block like phase.

Thus, studies have shown that several laser welding and some non-laser welding techniques, as well as brazing methods, have been and can be used to successfully join Ti_6Al_4V parts to each other and to certain dissimilar metals as well.

9. SHAPING BY MACHINING

Machining is one of the most important processes undergone by any material to form a component for various applications. Machining of titanium aluminium alloy had been a challenging task due to its heat properties and various factors like high tool wear etc.

Studies of defects and impurities present in Ti_6Al_4V and their effects on the properties and machining of the alloy is important. When this alloy is used to machine complex contours, especially for rocket engines, impurities in the alloy at cryogenic temperatures lead to a ductility diminishing. Different layers with varying chemical and structural properties were attained when diffusion occurs in the compaction cycle. Briott *et al.* [74] performed an analysis of these phases and conducted several mechanical tests to identify and characterize the defects present and fracture processes were proposed. Another study was performed on microdefects and 3D electron behavior in binary type Ti-Al alloys [75]. With a greater Al content, free electron density reduces but the open volume of grain boundary defects becomes larger, but with a greater Ti content, the contrary happens.

Since different machining methods could form a separate review by itself, and may be beyond the scope of this review, a brief analysis of how various machining methods are analyzed and chosen, is presented here.

9.1. Analysis by Chip Formation

Many researchers have used the chip formation for understanding the machining characteristics of Titanium alloys.

9.1.1. Saw Tooth Chip

One of the major characteristics in the machining of titanium alloys is the formation of saw tooth chip [76]. From micrographic observations segment spacing, "adiabatic shear band" (ASB) width and the degree of segmentation were evaluated. Based on the adiabatic shear sensitivity of workpiece materials the mechanism of saw tooth chip formation was studied at high strain rates. The microstructure inside the ASBs evolves from deformed band to a transformed band as the cutting speed increases. The catastrophic instability depending on the adiabatic shear sensitivity of the workpiece material was analyzed.

9.1.2. Serrated Chips

Another study was based on the formation of serrated chips [77]. This type of chip is formed during high efficiency cutting of the Ti_6Al_4V alloy. It is observed that the periodic high frequency serrated chip disturbs the cutting force and also hinders the surface integrity and the tool wear of the workpiece. On analyzing the frequency and geometric characteristics of the microstructure it was concluded that the cutting speed and feed rate have huge impact on the characteristics of the chip. The frequency of the serrated chip can be reduced by increasing the cutting depth, feed and lowering the speed. Some have attempted the study on friction model at the tool-chip interface [78]. Using cemented carbide tool KW10 in orthogonal turning of Ti_6Al_4V alloy, the cutting forces have been examined.

9.2. Impact of Cutting Edge Radius

Cutting edge radius has an influence over the cutting deformation in high speed machining of Ti_6Al_4V [79]. Factors like cutting temperature, equivalent stress distribution, the chip morphology and cutting deformation coefficient were also analyzed. It was observed that as the cutting edge radius increases, it exhibits a chip thinning effect. An important factor that affects the machining accuracy is the dynamic change in cutting force which is a cause for chatter formation [80].

9.3. Impact of Type of Abrasive

In another study, dry grinding conditions in milling machine XS5040 attached with belt grinding equipment were performed [81]. Properties like surface integrity of the alloy with zirconia alumina and SiC belts were examined. Using instruments like HXS-1000A and TALYSURF5, surface hardness for ground surface and microcosmic geometry was estimated. It was observed that zirconia alumina belt had better performance than SiC belt. It possesses small grinding affected zone (<15μm) and better surface quality.

9.4. Single Grain Grinding Test

In the study of high speed grinding mechanism, single-grain grinding test acts as an important part [82]. Using single CBN grain for high speed grinding test, a study on developing a new method was done. Prediction of optimum cutting conditions for a better process is necessary.

9.5. Mathematical Model

A study has been done on developing a mathematical model for predicting the tangential cutting force occurring in end milling. The impact of milling parameters and surface roughness was experimented in a study of side milling of titanium alloys [83]. The investigation also considers the factors like average cutting thickness, material removal rate and vibration. It is concluded that the surface roughness is directly proportional to the average cutting thickness. A study on seven milling cutters of TC4 (Ti_6Al_4V) were evaluated [84]. It shows that the averaged flank wear of each cutter is linearly proportional to the accumulated cutting length expansion.

Another study on deformations of selected types of milling cutters was performed [85]. The data obtained were used for finite element modeling of the cutters. These details were used in computing the machining errors for products made of Ti_6Al_4V. Electrical discharge machining (EDM) process is also a technique which is a favourable process for titanium alloy [86]. A study on an efficient EDM process with a bundled die-sinking electrode was experimented. On comparing the EDM process, it revealed its high performance by the use of multi-hole inner flushing to efficiently remove molten material from the inter-electrode gap and through the increased ability to apply a higher peak current.

9.6. Tool Life Prediction

One of the major factors that make the machining of the titanium aluminium alloy difficult is the high amount of tool wear that occurs during the process. Carbide tool is one of the most common tools that is employed to machine titanium-aluminium alloy. A study on optimizing cutting parameters was undertaken [87]. Based on the orthogonal turning tests on a CA6140 lathe the experimental functions of tool life were developed. The major mechanisms of wear found in the tool were adhesion, diffusion and micro-chipping and the tool wear morphologies were evaluated by scanning electron microscope (SEM) and energy disperse spectroscopy (EDS).

In dry turning of Ti_6Al_4V the larger depth of cut and lower cutting speed is the better selection for coated carbide. Based on the multi-variable linear regression analysis the experimental formula regressed was able to predict the tool life under certain conditions [88]. A study predicting the tool wear was carried out using neural network. As the tool life is different for different tool materials with varied cutting conditions under study, the wear prediction model is verified by further experiments [89]. The results reveal that the prediction model can meet the actual production as the relative error is less than 10%.

10. EVALUATING THE WEAR BEHAVIOUR

Tribology is the study of properties observed when surfaces are rubbed together or are in contact. Several methods are available to test the properties of Ti_6Al_4V during contact with various surfaces, and the effect of surface modification on the tribological properties of Ti_6Al_4V.

10.1. Thermochemical Methods

One method of improving the tribological properties of Ti_6Al_4V is by employing thermochemical techniques. One tested technique used is Triode plasma oxidation where three electrodes are used, the purpose of the third being to increase the levels of ionization present in the plasma. It was discovered that the surface obtained had an oxygen rich layer that was found to possess good surface hardness and adherence properties. The hardness was also found to decrease with the depth of treatment, and a harder and thicker layer was found to be formed in an environment with greater oxygen content, higher substrate temperature as well as increased current density [90].

10.2. Ball-on-Disc Method

Studies have also been made on the effect of surface modification by nitrogen ion implantation on the tribological properties of Ti_6Al_4V [53] as well as surface alloying on tribological properties, using borided Ti_6Al_4V [47] and plasma surface alloying technique [48]. These have already been discussed earlier in the article. Further tests using borides were conducted by depositing a film of titanium boride doped with carbon, containing an interlayer of silicon carbide, on the surface of Ti_6Al_4V [91]. Magnetron spluttering methods were used for depositing the layer on the alloy. There was observed to be good adhesion between the various layers, and when ball on disc tests were conducted using silicon nitride balls, in simulation body fluid, better properties of wear rate and frictional coefficient were discovered. This was attributed to the presence of doped carbon atoms.

10.3. Pin-on-Disc Method

As mentioned, TiNi is one of the chemicals used for surface modification of Ti_6Al_4V. An alloy created with this layer was analyzed for various surface properties and its tribological behavior was studied using the pin-on-disc test [92]. The results showed that TiNi layer displayed abrasion wear mechanism, whereas Ti_6Al_4V substrate displayed both abrasion as well as adhesion wear mechanisms, and the wear resistance of the alloyed layer was found to have increased substantially.

Pin-on-disc (rotating) tests can also be used to study the behavior of Ti_6Al_4V alloy disc when it slides against tungsten carbide cobalt pin in different gaseous media at room temperature-nitrogen and air [93]. The effect of nitrogen gas was to reduce the coefficient of friction as well as the wear of the testing surface of the pin and the disc, with different wear mechanisms observed for each surface. These tests can also be used to test the properties of various titanium alloys whose samples were created by mechanical milling and alloying processes. The samples were tested with varying sliding distances and loads. The Ti_6Al_4V sample tested was found to possess no porosity, but a slight level of ferrous adulteration resulting from the milling process. The hardness of Ti_6Al_4V was found to be lower than the sponge titanium sample, but the wear losses were also discovered to be lower, since Ti_6Al_4V lacked the porosity present in sponge titanium [94].

10.4. Nanotribometric Evaluation

Linear reciprocating sliding behavior of Ti_6Al_4V against alumina using nanotribometer contact was studied [95]. Ringer's solution was used as a medium for performing the experiment, while varying the load and speed, and the contact frictional behavior was investigated. Mathematical analysis and plots of dynamic friction coefficients were created, along with calculations of effective root mean square coefficient of friction. These analytical tools were used to determine behavior and wear mechanisms during different periods of sliding. Also, the wear process was continuously monitored with varying velocities and loads using an alternate technique [96]. The penetration depth parameter was recorded continuously and curves were plotted to analyze the wear mechanisms taking place, by comparing to the values obtained by examining the geometry of the worn surface. The conclusion drawn was that applied loads have a highly significant effect on the wear process.

Thus, thermochemical, pin-on-disc, ball-on-disc methods and mathematical modeling have been employed to observe the tribological behavior of Ti_6Al_4V. Also, the changes in wear resistance and frictional coefficients with modifications like titanium nitride, titanium boride, etc layers were studied and it was observed that the surface modification methods can be employed where an improvement in the tribological properties of this alloy is desired.

11. PROCESSING AND PROPERTY CORRELATION

Processing of titianium aluminium alloys is very important - since these alloys inherently have low thermal conductivity and are difficult to machine. The properties vary according to the processing method deployed. Various techniques have been employed and tested in recent years, which are briefly discussed below:

11.1. Mechanical Behavior

Since knowledge of mechanical behavior and properties are essential for the creation of computer models, Rossi *et al.* [97] conducted tests on Ti_6Al_4V alloy on its mechanical behavior with a focus on hardening and anisotropic properties. Standard shear, cyclic loading and plain strain uniaxial and biaxial tests were conducted and stress strain curves plotted. High Strain Rate Torsion and Bauschinger Tests on Ti_6Al_4V have also been conducted [98]. These experiments are essential for fast forming process re-creation and simulation. These quasi static tests, used to analyze the kinematic hardening of the alloy, require a fixed sample geometry for loading both forward and reverse. This is generally tough to realize practically. Torsion tests using Hopkinson's bar were performed to study the material behavior, since in torsion tests, higher strain rates than tensile tests can be attained due to absence of reduction in cross sectional area. Additionally a "split Hopkinsin's bar" had been created for the Bauschinger Tests and they were carried out using a reversible shear load. These methods were used to identify the kinematic behavior of the material, along with finite element simulations. Similar split bar Hopkinson's tests were conducted on a commercially available alloy, and testing was carried out to analyze the initial crystal structure influence on the mechanical properties, by testing in different directions [99]. These results were compared to numerical and theoretical results using a plasticity code, where twinning at boundary layers was considered a mode of active deformation.

11.2. Cooling Methods

Titanium alloys normally have a low thermal conductivity, and this property along with the chip formation tendency leads to high heat generation. These directly lead to tough machining conditions. Since cooling is essential to overcome these problems, various cooling methods were studied. High pressure cooling was found to be one of the most effective, and steps to manufacture the tool using proper lubrication and cooling methods were employed for the milling process carried out on Ti_6Al_4V [100]. These schemes have proved to be highly effective. Cooling methods influence the outcome of both the workpiece and the tool after machining. Different lubrication systems can be used for milling Ti_6Al_4V. Lubrication studies under conditions such as wet, MQL (Minimum Quantity Lubrication), dry and nitrogen gas jet were conducted [101]. The maximum effect of cooling changes were found in the cutting forces, but their impact on surface roughness was minimal. Smoother contact of the chip occurred with the use of nitrogen gas, accompanied by adsorption of nitrogen.

11.3. Laser Cutting and Processing

When these alloys are machined surface properties are changed in the zone of machining due to low thermal conductivity of the alloy, as well as high chemical reactivity. Studies were conducted on laser cutting using a fiber laser (2 kW) in continuous wave mode. Argon gas was used as a cutting medium. 1 mm thick sheets were cut, and the altered properties of the cut zone were investigated [102]. Once laser processing was conducted on Ti_6Al_4V, torsional tests were conducted on samples of different porosities to test the deformation and mechanical behavior of the samples [34]. It was found that greater the porosity, lesser the yield strength and modulus. It was concluded from these series of tests that the brittleness ingrained in such samples can be mitigated using laser processing and thus can be used successfully in implants subjected to loading.

11.4. Plasma Electrolytic Oxidation

A study was also conducted on the effect of plasma electrolytic oxidation of Ti_6Al_4V under single-pulse power supply using electrochemical impedance spectroscopy and transient waveform analysis [27]. In a constant density electrolyte environment, the changes in termination voltage induced a corresponding change in coating structure. Another phenomenon observed was "at the beginning pulse, across the breakdown coating, a charging process occurred". Surface effects of micro arc oxidation of Ti_6Al_4V were also conducted in $(CH3COO)_2Ca.H_2O$ + Na_3PO_4 electrolyte [103]. A porous titanium oxide layer on the surface of the alloy was formed, along with a hydroxyapatite and calcium titanate coating. When the electrolyte concentration was raised, the wettability and surface roughness reduced, and the pores vanished.

11.5. Argon Gas Atomization

Using argon gas atomization, powders of Ti_6Al_4V alloy were created and the pre-alloyed properties were studied [104]. The powdered particles were found to be spherical, with a hexagonal cellular structure and a martensite phase as a result of the solidification at high rates taking place in this process. After Hot Isostatic Pressing was carried out, the samples were found to possess a Widmanstaten microstructue characterized by a continuous grain boundary. Tensile stress analysis concluded that there is evident brittle clevage fracture in the sample.

11.6. Forging with Protective Coating Layer

A technique was invented to forge a titanium alloy by coating with a protective material [105]. Before high temperature forging is carried out, a borosilicate glass lubricant was coated on top of the protective aluminide based coating. This method can be used to forge high temperature and pressure components of gas turbines.

11.7. Highly Reflective Coating

An aluminum and titanium alloy was created with high specular reflectivity, resistant to oxidation and corrosion and possessing adhesion to polymer materials that could be used as a mirror [106]. This alloy can be a reflective coating of micrometer range thickness with a polymer protective film covering it. A polymer material layer supports the reflective coating.

11.8. Reinforcing with TiB Whiskers

Ti_6Al_4V was reinforced with TiB whiskers and extruded and heat treatment was carried out [107]. This was done in order to improve the mechanical properties. A detailed microstructural study was undertaken. The equiaxed network architecture that existed was extruded into column network type architecture. The tests confirmed that the mechanical properties like elasticity, strength, ductility were improved by the extrusion process. Once the hot extrusion deformation is complete, aging and water quenching improves the strength further. The elastic modulus of the as sintered composites follows the upper bound of Hashin-Shtrikman (H-S) theory before extrusion. The elastic modulus of the as-extruded composites agrees well with the prediction from Halpin-Tsai equation.

11.9. Thermohydrogen Processing: Titanium Aluminium Alloy at Elevated Temperatures

Analyzing high temperature properties of alloys is an important study as we widely use the study on isothermal compression of hydrogenated Ti_6Al_4V alloy at a strain rate 3×10?3 s?1 was carried out. Effect of a simplified thermohydrogen processing (THP) was assessed on compression behavior. The results revealed that the flow stress and deformation temperature was reduced significantly. It also improves the strain rate sensitivity index. The reason behind the improvement of formability of the alloy is the increasing amount of β phase and the ultrafine and equiaxial microstructure precipitated between the original α or β laths [108].

11.10. Shear Testing

A study on evaluating the shear behavior of sheet metals over a wide range of strain rates was carried out. Using traditional tensile test this technique was developed. The main objectives during the development of the shear specimen have been 1) obtaining a homogeneous stress state with low stress triaxiality in the zone of the sample subjected to shear and 2) appropriateness for dynamic testing. Dynamic tests exhibited practical constraints where the specimen is loaded by mechanical waves in a split Hopkinson tensile bar device. When this technique was applied to Ti_6Al_4V sheet, both numerical and experimental results were similar [109].

11.11. Microsphere Sintering

Porous samples of Ti_6Al_4V were created by microsphere sintering [110]. Using moulds of different materials, including zirconia, alumina, stoneware and yttria and microspheres of different dimensions, samples were created and observed. It was found that the smallest microspheres had the best mechanical properties desired, and the stiffness was discovered to be much lower than the value of stiffness in half the bulk material.

11.12. FEM Simulation

Finite element simulation is a popular technique used to analyze the experimental results which has reduced the cost considerably. Various studies were performed based on Johnson-Cook's (JC) constitutive model which describes the material behavior [111]. A study based on the plastic strain energy and fracture criterion combining the effect of different fracture mechanisms are proposed to model the progressive damage and fracture, respectively. Simulated results on prediction of chip morphology were similar to the experimental results. Another study on the material model parameters of JC equation was performed [112]. This paper has dealt with the performance of four material model sets of the equation. The results reveal that the stress, strain and temperature had an excellent prediction but there were slight deviation in cutting force and chip morphology.

Chip formation is an important factor that had been studied to improve the process parameters for better machining. A study on segmented chip which is formed during low cutting speeds and persists even at high speed [113]. The mechanism of catastrophic shear instability during orthogonal cutting of Ti_6Al_4V alloy was investigated.

A study reports on the process parameter prediction by Finite Element Method of laser clad TiC/NiCrBSiC coatings [114]. As the laser power increases, the temperature distribution was enlarged. The results were in good agreement with the theoretical results. Studies on shear test techniques were also carried out [115]. Torsion of thin-walled tubes, compression of hat-shaped specimens and tension of planar shear specimens are the three tests performed which are known to be complementary to each other.

A study on the residual stresses induced during turning was carried out [116]. Using ABAQUS FE code the micro-scale residual stresses were formulated into axisymmetric FE models. The compressive and the residual stresses measured are in good agreement with the predicted results.

Various studies on the modeling for calculating the process parameters have been reported. A finite element model to simulate the formation of continuous or discontinuous chips depending upon the conditions were developed [117]. Factor like yield stress is taken as a function of strain, strain rate and the temperature. Dynamic effects, constitutive damage law, thermo-mechanical coupling, constitutive damage and contact friction are also taken into account. The effect of temperature field of laser re-melting, plasma sprayed, Ni-based gradient coating on Ti_6Al_4V alloy surface to obtain evolution law has been reported [118]. The effects like heat conduction, heat radiation, heat convection, phase change, non-linearity on coatings and substrate are also considered in this study. The results show that the mechanical bonding changes to metallurgical bonding.

CONCLUSION

The use of Ti_6Al_4V as a bio material has been reviewed.

The evaluation of this material's bio compatibility, additive manufacturing processes like Laser melting and property improvement by coatings and surface alloying are presented. Improving the machinability and improving the mechanical properties by heat treatment are discussed. Shaping by joining like welding and brazing, and shaping by machining are discussed. Evaluating the wear behaviour and the impact on processing method on its property are presented. The various studies for converting Ti_6Al_4V as a useful material for biomedical applications are consolidated in Table **1**. The following are the immediate learnings:

- Electron beam melting can enhance properties of Ti_6Al_4V scaffold. Stem cells help in growth of tissue. Metallic scaffolds combined with stem cell has good possibility. Roughening the surface of the scaffold with blasting improves cell growth and corrosion properties. Electron Beam Melting improves attachment to biological cells.
- By osteointegration - by mineralizing the surface with calcium apatite it is possible to improve the interaction between bone and alloy. Growing osteoblasts on Ti_6Al_4V surface gives better phenotypes, resulting in increased bone formation and reduced healing time.
- The surface area of the implant material can be increased by blasting with particles of Al_2O_3, SiO_2 and ZrO_2. This leads to an increase in the surface roughness, thereby providing a literally larger surface area.
- Coarse particle blasting and laser gas nitriding improve the corrosion resistance.
- Surface texturing with Fiber lasers have been used for adhesion to dental implants.
- Chemical treatment in an alkali solution, in a mixture of NH_4F and H_3PO_4 and Ca-P pre-coating before collagen coating can help in altering the bioactivity.
- Formation of hydroxyapatite layer on the surface by various methods; TiN reinforced composite coatings, arc ion plating (AIP) CrN coatings and Surface alloying by Double glow plasma method can improve the wear resistance and adhesion properties.
- Altering the voltage applied for the treatment of the alloy can inhibit bacterial growth.
- Joint fluid aeration, choosing a proper microstructure

Table 1. Consolidated data on studies on Ti_6Al_4V.

Property Studied	Approach	Reference
Improving attachment to biological Cells	Growing osteoblasts on Ti_6Al_4V surface gives better phenotypes, resulting in increased bone formation and reduced healing time.	[2]
	By Electron Beam Melting.	[3]
Corrosion resistance	Improving the surface area by increasing the surface roughness by blasting with particles Al_2O_3, SiO_2 and ZrO_2. Coarse particle blasting lead to spherical oxide layer formation and increased corrosion resistance.	[4]
	Laser gas nitriding.	[54]
Wettability	Varying the surface roughness and by UV irradiation (negative correlation observed).	[5]
Adhesion to dental implants	Surface texturing with Fiber lasers.	[6]
Altering the bioactivity	Chemical treatment in an alkali solution, in a mixture of NH_4F and H_3PO_4.	[7]
	Ca-P precoating before collagen coating.	[8]
Improving the wear resistance and adhesion properties	Formation of hydroxyapatite layer on the surface by various methods.	[11, 12]
	TiN reinforced composite coatings.	[17]
	Arc ion plating (AIP) CrN coatings and also their tribological properties.	[37]
	Surface alloying by Double glow plasma method.	[46]
Inhibiting bacterial growth	By altering the voltage applied for the treatment of the alloy.	[13]
Preventing degradation of hip implants	Joint fluid aeration, choosing a proper microstructure of the material as well as making sure the mating surfaces have proper tolerance values.	[14]
Improving the interaction between bone and alloy	By osteointegration - by mineralizing the surface with calcium apatite.	[15]
Improving the compressive strength and hardness	Boron additions on TiC/Ti_6Al_4V composites.	[20]
Lower porosity and higher density parts	Selective laser melting.	[21, 22]
Improved surface hardness	Cryogenic treatment on porous parts.	[25, 26]

of the material as well as making sure the mating surfaces have proper tolerance values, prevent degradation of hip implants.

- Boron additions on TiC/Ti_6Al_4V composites can improve the compressive strength and hardness.
- Selective Laser Melting can be used to fabricate parts by additive manufacturing techniques with almost same density as bulk Ti_6Al_4V. Cryogenic treatment on porous parts can improve the surface hardness.
- Titanium-metal-matrix composites with enhanced strengths can be formed either by HIP (Hot Isostatic pressing) or by co-rolling with SiC filaments in between sheets of Ti_6Al_4V.
- Using laser processing, the brittleness in porous materials could be mitigated.
- Diamond like carbon coatings can enhance tribocorrosion properties.
- High temperature wear properties and lubricating properties could be achieved by molybdenising the surface.
- Machining of Ti_6Al_4V is quite difficult. Many methods of how to optimise machining using Finite element techniques are reported and can be utilised.

It is believed that these details will serve as a starting point for any researcher who wants to study the use of Ti_6Al_4V for biomedical applications.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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REFERENCES

[1] Narayanan R, Seshadri SK, Kwon TY, Kim KH. Electrochemical nano-grained calcium phosphate coatings on Ti_6Al_4V for biomaterial applications. Scri Mater 2007; 56(3): 229-32.

[2] Olivares-Navarrete R, Hyzy S, Schneide J, *et al*. Microstructured Ti_6Al_4V surfaces increase osteoblast maturation and regulate BMP signaling pathway GP25. Spine Journal Meeting October 2011, ISSLS Society Meeting Abstracts 2011.

[3] De Peppo GM, Palmquist A, Borchardt P, *et al*. Free-form-fabricated commercially pure Ti and Ti_6Al_4V porous scaffolds support the growth of human embryonic stem cell-derived mesodermal progenitors. Sci World J, 2012; 2012: Article ID 646417.

[4] Barranco V, Escudero ML, Garcia-Alonso MC. Influence of the microstructure and topography on the barrier properties of oxide scales generated on blasted Ti_6Al_4V surfaces. Acta Biomater 2011; 7(6): 2716-25.

[5] Ching-Cheng W, Yi-Hsien H. Correlation of UV irradiation-induced wettability characteristics by factorial design of experiments on Ti_6Al_4V. Int J Phys Sci 2011; 6(19): 4585-94.

[6] Erdoan M, Öktem B, Kalaycolu H, *et al.* Texturing of titanium (Ti_6Al_4V) medical implant surfaces with MHz-repetition-rate femtosecond and picosecond Yb-doped fiber lasers. Opt Express 2011; 19(11): 10986-96.

[7] Lukacova H, Plesingerova B, Vojtko M. Bioactivity of chemical, electrochemical and thermal treatment of Ti_6Al_4V. Acta Metall Slovaca 2011; 17(1): 11-7.

[8] Wang RCC, Hsieh MC, Yang SP, *et al.* Characteristics and cyto-compatibility of collagen/Ca-P coatings on Ti_6Al_4V substrate. Surf Coat Technol 2011; 205(19): 4683-9.

[9] Li H, Zheng Y, Lin J. Comparative evaluation on the *in vitro* biological performance of $Ti_{45}Al_{8.5}Nb$ intermetallic with Ti_6Al_4V and Ti_6Al_7Nb alloys. Adv Eng Mater 2011; 13(5): 187-93.

[10] Demczuk A, Swieczko-Zurek B, Ossowska A. Corrosion resistance examinations of Ti_6Al_4V alloy with the use of potentiodynamic method in Ringer's and artificial saliva solutions. Adv Mater Sci 2011; 11(4): 35-42.

[11] Vangoelue SY, Bayrak O, Kovaci H, Yildirim OS, Akguen A, Ayhan C. Investigation of the pull-out strengths of Ti_6Al_4V cortical screws oxidized with various methods. J Biomech 2011; 44(1): 5.

[12] Vangolu Y, Alsaran A, Yildirim OS. Wear properties of micro arc oxidized and hydrothermally treated Ti_6Al_4V alloy in simulated body fluid. Wear 2011; 271(9-10): 2322-7.

[13] Giordano C, Saino E, Rimondin L, *et al*. Electrochemically induced anatase inhibits bacterial colonization on Titanium Grade 2 and Ti_6Al_4V alloy for dental and orthopedic devices. Colloids Surf B Biointerfaces 2011; 88 (2): 648-55.

[14] Chandra A, Ryu JJ, Karra P, *et al.* Life expectancy of modular Ti_6Al_4V hip implants: influence of stress and environment. J Mech Behav Biomed Mater 2011; 4(8): 1990-2001.

[15] Liu P, Smits J, Ayers DC, Song J. Surface mineralization of Ti_6Al_4V substrates with calcium apatites for the retention and local delivery of recombinant human bone morphogenetic protein. Acta Biomater 2011; 7(9): 3488-95.

[16] Przybyło MW, Klimek L, Okroj W, *et al*. Adhesion, activation, and aggregation of blood platelets and biofilm formation on the surfaces of titanium alloys Ti_6Al_4V and Ti_6Al_7Nb. J Biomed Mater Res: Part A 2012; 100A (3): 768-75.

[17] Balla VK, Bhat A, Bose S, Bandyopadhyay A. Laser processed TiN reinforced Ti_6Al_4V composite coatings. J Mech Behav Biomed Mater 2012; 6: 9-20.

[18] Testani C, Ferraro F, Deodati P, *et al.* Comparison between roll diffusion bonding and hot isostatic pressing production processes of Ti_6Al_4V-SiC_f metal matrix composites. Mater Sci Forum 2011; 678: 145-54.

[19] Deodati P, Donnini R, Kaciulis S, *et al.* Micro-chemistry and mechanical behaviour of Ti_6Al_4V-SiC_f composite produced by hip for aeronautical applications. Mater Sci Forum 2011; 78: 23-47.

[20] Xiang W, Xuliang M, Xinlin L, Lihua D, Mingjia W. Effect of boron addition on microstructure and mechanical properties of TiC/Ti_6Al_4V composites. Mater Des 2012; 36: 41-6.

[21] Song B, Dong S, Zhang B, Liao H, Coddet C. Effects of processing parameters on microstructure and mechanical property of selective laser melted Ti_6Al_4V. Mater Des 2012; 35: 120-5.

[22] Song B, Dong S, Liao H, Coddet C. Process parameter selection for selective laser melting of Ti_6Al_4V based on temperature distribution simulation and experimental sintering. Int J Adv Manuf Technol 2012; 61 (9-12): 967-74.

[23] Bael SV, Kerckhofs G, Moesen M, Pyka G. Micro-CT-based improvement of geometrical and mechanical controllability of selective laser melted Ti_6Al_4V porous structures. Mater Sci Eng A 2011; 528(24): 7423-31.

[24] Balla VK, Martinez S, Rogoza BT, *et al.* Quasi static torsional deformation behavior of porous Ti_6Al_4V alloy. Mater Sci Eng C 2011; 31(5): 941-9.

[25] Zielinskia A, Jażdżewska M, Narożniak-Luksza A, Serbiński W. Surface structure and properties of Ti_6Al_4V - alloy laser melted at cryogenic conditions. J Achievements Mater Manuf Eng 2006; 18(1-2): 423-6.

[26] Zielinski A, Jażdżewska M, Lubinski J, Serbinski W. Effects of laser remelting at cryogenic conditions on microstructure and wear resistance of the Ti_6Al_4V alloy applied in medicine. Solid State Phenomena 2012; 183: 215-24.

[27] Zhang X, Yao Z, Jiang Z, Zhang Y, Liu X. Investigation of the plasma electrolytic oxidation of Ti_6Al_4V under single-pulse power supply. Corros Sci 2011; 53(6): 2253-62.

[28] Arslan E, Totik Y, Efeoglu I. The investigation of the tribocorrosion properties of DLC coatings deposited on Ti_6Al_4V alloys by CFUBMS. Prog Org Coat 2012; 74(4): 768-71.

[29] Chen F, Chen JQ, Zhou H, Li CM. DLC films synthesized on the Ti_6Al_4V alloy surface by plasma gun at an atmospheric pressure. Mater Sci Forum 2011; 687: 739-44.

[30] Nibennanoune Z, George D, Antoni F, *et al.* Improving diamond coating on Ti_6Al_4V substrate using a diamond like carbon interlayer: raman residual stress evaluation and AFM analyses. Diam Relat Mater 2011; 22: 105-12.

[31] Guan X, Lu Z, Wang L. Achieving high tribological performance of graphite-like carbon coatings on Ti_6Al_4V in aqueous environments by gradient interface design. Tribol Lett 2011; 44 (3): 315-25.

[32] Ben NJ, Liang WP, Ren BL, Miao Q. Tribological behaviors of Ti_6Al_4V with surface plasma molybdenized. Mater Sci Forum 2012; 704-705: 1253-8.

[33] Qin L, Yang KK, Wang S, Tang B. Repeated impact resistance of Cr-Mo surface alloying layers on Ti_6Al_4V alloy. Adv Mat Res 2012; 399-401: 1958-61.

[34] Panjwani B, Satyanarayana N, Sinha SK. Tribological characterization of a biocompatible thin film of UHMWPE on Ti_6Al_4V and the effects of PFPE as top lubricating layer. J Mech Behav Biomed Mater 2011; 4(7): 953-60.

[35] Balcaen Y, Radutoiu N, Alexis J, *et al.* Mechanical and barrier properties of MOCVD processed alumina coatings on Ti_6Al_4V titanium alloy. Surf Coat Technol 2011; 206(7): 1684-90.

[36] Teng YY, Chen Q, Xin L. The effect of coatings on the cyclic oxidation behaviour of Ti_6Al_4V at 750°C. Adv Mat Res 2012; 393-395: 428-35.

[37] Chang ZK, Wan XS, Pei ZL, Gong J, Sun C. Microstructure and mechanical properties of CrN coating deposited by arc ion plating on Ti_6Al_4V substrate. Surf Coat Technol 2011; 205(19): 4690-6.

[38] Mann BS, Arya V, Pant BK. Cavitation erosion behavior of HPDL-treated TWAS-coated Ti_6Al_4V alloy and its similarity with water droplet erosion. J Mater Eng Perform 2012; 21(6): 849-53.

[39] Yang ZY, Xia LQ, Sun WW, Li WJ. Effect of surface characteristics on bioactivity of ceramic coating on Ti_6Al_4V by plasma electrolytic oxidation. Adv Mat Res 2011; 320: 33-7.

[40] Zhou H, Lawrence JG, Touny AH, Bahduri SB. Biomimetic coating of bisphosphonate incorporated CDHA on Ti_6Al_4V. J Mater Sci Mater Med 2012; 23(2): 365-74.

[41] Qi GC, Zhang S, Li Q, *et al*. Magnesium incorporation in sol-gel derived apatite coating on Ti_6Al_4V substrate. Adv Mat Res 2011; 299-300: 448-51.

[42] Yanovska A, Kuznetsov V, Stanislavov A, Danilchenko S, Sukhodub L. Synthesis and characterization of hydroxyapatite-based coatings for medical implants obtained on chemically modified Ti_6Al_4V substrates. Surf Coat Technol 2011; 205(23-24): 5324-9.

[43] Peng C, Wei Q, Deng JY, Ping RT, Li XY. Preparation and characterization of bone-like apatite coating on Ti_6Al_4V spinal fusion devices. Adv Mat Res 2011; 311-313: 1722-7.

[44] Singh G, Singh S, Prakash S. Surface characterization of plasma sprayed pure and reinforced hydroxyapatite coating on Ti_6Al_4V alloy. Surf Coat Technol 2011; 205(20): 4814-20.

[45] Aral A, Gunyuz M, Baydogan M, Karaguler NG, Olcay E, Cimenoglu H. Anti-bacterial microporous ceramic coating for Ti_6Al_4V alloys. Key Eng Mater 2011; 493-494: 916-9.

[46] Tang CB, Liu DX, Li FQ, Tang B, Qin L. Improvement in wear and corrosive wear resistance of Ti_6Al_4V alloy by double glow plasma surface alloying with W-Mo and W-Mo-N. Mater Sci Forum 2011; 675-677: 1253-7.

[47] Atar E, Kayali ES, Cimenoglu H. Friction and wear behaviour of borided Ti_6Al_4V alloy sliding against Al_2O_3 and Si_3N_4 balls in water. Defect Diffus Forum 2011; 312-315: 1004-9.

[48] Wang Z, He Z, Wang Y, Liu X, Tang B. Microstructure and tribological behaviors of Ti_6Al_4V alloy treated by plasma Ni alloying. Appl Surf Sci 2011; 257(23): 10267-72.

[49] Makama Z, Doble I, Nicolson D, *et al.* Surface preparation of stainless steel 316L, bronze CW451K and titanium Ti_6Al_4V for bonding to polyurethane in marine cable connector assemblies. Trans Inst Metal Finish 2011; 89(5): 237-43.

[50] Savonov GS, Ueda M, Oliveira RM, Otani C. Electrochemical behavior of the Ti_6Al_4V alloy implanted by nitrogen PIII. Surf Coat Technol 2011; 206 (7): 2017-20.

[51] Oliveira RM, Mello CB, Silva G, Gonçalves JAN, Ueda M, Pichon L. Improved properties of Ti_6Al_4V by means of nitrogen high temperature plasma based ion implantation. Surf Coat Technol 2011; 205 (2): S111-4.

[52] Feng X, Sun M, Ma X, Tang G. Structure and tribological performance by nitrogen and oxygen plasma based ion implantation on Ti_6Al_4V alloy. Appl Surf Sci 2011; 257(23): 9904-8.

[53] Shokouhy A, Ghoraneviss M, Larijani MM, Yari M, Haji Hosseini SH, Eshghabadi M. Modification of Ti_6Al_4V corrosion property by nitrogen ion implantation. J Fusion Energy 2011; 30(5): 437-41.

[54] Zhang CH, Tang LW, Hu F, Zhang S, Man HC. Study on wear and corrosion properties of Ti_6Al_4V alloy by laser gas nitriding. Adv Mat Res 2011; 299-300: 188-92.

[55] Regener B, Krempaszky C, Werner E, Stockinger M. Modelling the micromorphology of heat treated Ti_6Al_4V forgings by means of spatial tessellations feasible for FEM analyses of microscale residual stresses. Comput Mater Sci 2012; 52(1): 77-81.

[56] Mutombo K, Rossouw P, Govender G. Mechanical properties of mill-annealed Ti_6Al_4V investment cast. Mater Sci Forum 2011; 690: 69-72.

[57] Dąbrowski R. The kinetics of phase transformations during continuous cooling of the Ti_6Al_4V alloy from the single-phase β range. Arch Metall Mater 2011; 56(3): 703-7.

[58] Mastrocinque E, Corrado G, Caiazzo F, Pasquino N, Sergi V. Effect of defocusing on bead-on-plate of Ti_6Al_4V by Yb: YAG disk laser. Adv Mat Res 2011; 383-390: 6258-64.

[59] Liu H, Nakata K, Yamamoto N, Liao J. Microstructural characteristics and mechanical properties in laser beam welds of Ti_6Al_4V alloy. J Mater Sci 2012; 47(3): 1460-70.

[60] Serroni G, Bitondo C, Astarita A, *et al.* A comparison between mechanical and electrochemical tests on Ti_6Al_4V welded by LBW. The 14th International Esaform Conference on Material Forming ESAFORM 2011, AIP Conference Proceedings 2011; 1353: 1391-6.

[61] Fan Y, Shipway P, Tansley G. Study of effect on tensile stress test from distortion of fiber laser welded Ti_6Al_4V using FEA. Adv Mat Res 2011; 314-316: 1889-94.

[62] Fan Y, Shipway PH, Tansley GD, Xu J. The effect of heat treatment on mechanical properties of pulsed Nd: YAG welded thin Ti_6Al_4V. Adv Mat Res 2011; 189-193: 3672-7.

[63] Casavola C, Pappalettere C, Tursi F. Residual stress on Ti_6Al_4V hybrid and laser welded joints. Engineering Applications of Residual Stress, Conference Proceedings of the Society for Exp Mech Series 2011; 8: 111-8.

[64] Brandizzi M, Mezzacappa C, Tricarico L, Satriano AA. Optimization of Ti_6Al_4V titanium alloy laser-arc hybrid weld parameters. Welding Int 2012; 26(12): 901-9.

[65] Brandizzi M, Satriano AA, Sorgente D, Tricarico L. Laser-arc hybrid welding of Ti_6Al_4V titanium alloy: mechanical characterization of joints and gap tolerance. Welding Int 2013; 27(2): 113-20.

[66] Tomashchuk I, Sallamand P, Andrzejewski H, Grevey D. The formation of intermetallics in dissimilar Ti_6Al_4V /copper/AISI316L electron beam and Nd: YAG laser joints. Intermetallics 2011; 19(10): 1466-73.

[67] Wang J, Cheng J, Bai P, Li Y. Investigation of joining Al-C-Ti cermets and Ti_6Al_4V by combustion synthesis. Mater Sci Eng B 2012; 177(19): 1703-6.

[68] Liu PT, Ren RM, Zhang TC, Ju DY. Numerical simulation and experiment of linear friction welding process of Ti_6Al_4V Alloy. Mater Sci Forum-Adv Mater Sci Technol 2011; 675-677: 925-8.

[69] Ju D, Liu P, Ren R. Thermo-mechanical simulation and experimental verification of linear friction welding process of Ti_6Al_4V alloy. [PDF] Available from: http: //www.yumpu.com/en /document/view/5944759/thermo-mechanical-simulation-and-expe rimental-fswp2012

[70] Wang F, Williams S, Rush M. Morphology investigation on direct current pulsed gas tungsten arc welded additive layer manufactured Ti_6Al_4V alloy. Int J Adv Manuf Technol 2011; 57(5-8): 597-603.

[71] Bao JC, Zhao J, Li JP. Fatigue property of welded joints of Ti_6Al_4V titanium alloy in corrosion environment. App Mech Mater-Mech Electron Eng III; 2011; 130-134: 1062-5.

[72] Zhu Z, Lee KY, Wang X. Ultrasonic welding of dissimilar metals, AA6061 and Ti_6Al_4. Int J Adv Manuf Technol 2012; 59: 569-74.

[73] Ma Z, Zhao W, Yan J, Li D. Interfacial reaction of intermetallic compounds of ultrasonic-assisted brazed joints between dissimilar alloys of Ti_6Al_4V and Al_4Cu_1Mg. Ultrason Sonochem 2011; 18(5): 1062-7.

[74] Briottet L, Scheer N, Guichard D. Fracture process of PM Ti_6Al_4V at 20 K in presence of impurities. ICF 2010, Honolulu, Hawaii. [PDF] Available from: http://www.gruppofrattura.it/ocs/index.php/ICF/IC F10/paper/viewFile/4735/6742

[75] Deng W, Guo XL, Xie B, Xiong DK, Huang YY. The 3D electrons and microdefects in binary Ti-Al alloys studied by positron Annihilation. J Adv Mat Res-New Materials, Applications and Processes 2011; 399-401: 99-102.

[76] Wana ZP, Zhub YE, Liuc HW, Tanga Y. Microstructure evolution of adiabatic shear bands and mechanisms of saw-tooth chip formation in machining Ti_6Al_4V. Mater Sci Eng: A 2012; 531: 155-63.

[77] Yang SC, Zheng ML, Zhang DQ, Liu N, Fan YH. Influence of cutting parameters on characteristics of serrated chip when high-efficiency cutting Ti_6Al_4V. Solid State Phenomena-Application of Diam Relate Mater 2011; 175: 278-83.

[78] Yuan YF, Chen WY. Study on determination of friction model at the tool-chip interface of titanium alloy Ti_6Al_4V based on orthogonal cutting. App Mech Mater-Materials and Comput Mech 2011; 117-119: 1788-91.

[79] Yang SC, Zheng ML, Fan YH, Zhang DQ, Li YB. Influences of cutting edge radius on cutting deformation in high-speed machining Ti_6Al_4V. Adv Mat Res-Progress in Manuf Autom Technol 2011; 305: 47-52.

[80] Patwari AU, Nurul Amin AKM, Faris WF. Statistical approach for the development of tangential cutting forcemodel in end milling of Ti_6Al_4V. Adv Mat Res-Adv Mater Process Technol II 2011; 264-265: 1160-5.

[81] Huo WG, Xu JH, Fu YC, Qi HJ. Investigation of surface quality on dry belt grinding of Ti_6Al_4V Alloy. Mater Sci Forum-Manuf Sci Technol XIV 2011; 697-698: 133-6.

[82] Tian L, Fu YC, Ding WF, Xu JH, Su HH. Removal mechanism of titanium alloy Ti_6Al_4V based on single-grain high speed grinding test. Key Eng Mater-Adv Grinding and Abrasive Technol XVI 2011; 487: 39-43.

[83] Liu H, Wu CH, Chen RD. Effects of cutting parameters on the surface roughness of Ti_6Al_4V titanium alloys in side milling. Solid State Phenomena-Application of Diam Relat Mater 2011; 175: 289-93.

[84] Lai JY, Li LX, Wu CH. Wear of milling cutters in machining of TC_4 (Ti_6Al_4V) titanium alloys. Solid State Phenomena-Application of Diam Relat Mater 2011; 175: 326-9.

[85] Kawalec A, Magdziak M. Deformations of selected milling cutters while milling Ti_6Al_4V alloy on a CNC machine tool, experimental tests and FEM modeling. Adv Manuf Sci Technol 2011; 35(4): 19-31.

[86] Gu L, Li L, Zhao W, Rajurkar KP. Electrical discharge machining of Ti_6Al_4V with a bundled electrode. Int J Machine Tools Manuf 2012; 53: 100-6.

[87] Wang XQ, Ai X, Zhao J, Fu XL, Pan YZ. Tool life prediction and cutting parameter optimization for coated carbide in Ti_6Al_4V turning. Adv Mat Res-Adv Mater Manuf Technol I 2012; 426: 186-9.

[88] Yuan YF, Chen WY, Zhang WY. Experimental study on tool wear in cutting titanium alloy Ti_6Al_4V. Adv Mat Res-Adv Mat 2011; 239-242: 2011-4.

[89] Fan YH, Zheng ML, Cheng MM, Zhang DQ. Tool wear prediction when machining Ti_6Al_4V using different tool materials. Adv Mat Res-High Speed Machining 2011; 188: 325-9.

[90] Banfield S, Wilson JCA, Cassar G, Leyland A, Matthews A, Housden J. An investigation into the effect of Triode Plasma Oxidation (TPO) on the tribological properties of Ti_6Al_4V. Surf Coat Technol 2011; 206(7): 1955-62.

[91] Xu XJ, Sheng XL, Chen D, Xin XL, Tian K, Yu CH. Friction/wear behaviors of magnetron sputtered TiB_2-C composite films on Ti_6Al_4V alloy substrate. Adv Mat Res-Manuf Process Technol 2011; 189- 193: 979-82.

[92] Wang ZX, He ZY, Wang YQ, Liu XP, Tang B. Study on tribological performance of the TiNi modified layer on the surface of the Ti_6Al_4V alloy. Mater Sci Forum-Funct Electron Mater 2011; 687: 759-64.

[93] Zhao W, He N, Li L. Friction and wear properties of WC-Co cemented carbide sliding against Ti_6Al_4V alloy in nitrogen gas. Adv Mat Res-High Speed Machining 2011; 188: 49-54.

[94] Ozyurek D, Tekeli S. Wear properties of titanium and Ti_6Al_4V titanium alloy by mechanical milling. High Temp Mater Process 2011; 30(1-2): 175-80.

[95] Zivic F, Babic M, Mitrovic S, Todorovic P. Interpretation of the friction coefficient during reciprocating sliding of Ti_6Al_4V alloy against Al_2O_3. Tribol Ind 2011; 33(1): 36-42.

[96] Zivic F, Babic M, Mitrovic S, Vencl A. Continuous control as alternative route for wear monitoring by measuring penetration depth during linear reciprocating sliding of Ti_6Al_4V alloy. J Alloys Compd 2011; 509(19): 5748-54.

[97] Rossi B, Gilles G, Zolotas E, Habraken A. Experimental investigations of the material behavior of Ti_6Al_4V titanium alloy. 2011. Available from: http://hdl.handle.net/2268/108591

[98] Peirs J, Verleysen P, Verbeken K, Coghe F, Degrieck J. High strain rate torsion and Bauschinger tests on Ti_6Al_4V. Mater Sci Forum 2012; 706-709: 774-9.

[99] Coghe F, Tirry W, Peirs J, *et al.* Comparison of experimental and numerical results for the quasi-static and dynamic tensile behaviour of a commercial Ti_6Al_4V alloy as a function of initial. Mater Sci Forum 2012; 706-709: 723-8.

[100] Hammond DR, Koen D, Oosthuizen GA. The investigation of a focused high pressure cooling technique for the milling of Ti_6Al_4V: ISEM 2011 Proceedings, September 21-23, Stellenbosch, South Africa. Available from: http://isem.org.za/index.php/isem/isem2011/paper/view/27/100

[101] Yong H, Sun YJ, Ge MJ, Li JF, Sun J. Milling experimental investigation on titanium alloy Ti_6Al_4V under different cooling/ lubrication conditions. Adv Mat Res-Adv Abrasive Technol XIV 2011; 325: 406-11.

[102] Scintilla LD, Sorgente D, Tricarico L. Experimental investigation on fiber laser cutting of Ti_6Al_4V thin sheet. Adv Mat Res-Adv Mater Process Technol II 2011; 264-265: 1281-6.

[103] Gunyuz M, Baydogan M, Cimenoglu H, Kayali ES. The effect of micro arc oxidation process parameters on surface properties of Ti_6Al_4V alloy. Defect Diffus Forum-Diffusion in Solids and Liquids VI 2011; 312-315: 1000-3.

[104] Liu N, Li Z, Yuan H, Xu WY, Zhang Y, Zhang GQ. Powder metallurgical processing of Ti_6Al_4V alloy. Adv Mat Res-High Perform Struct Mater Eng 2011; 217-218: 1336-42.

[105] Voice WE. Method of forging a titanium alloy. United States Patent US 7320238, 2008 January, 22.

[106] Martin M, Faverjon F, Moreau J, Poirson JM, Terrat JP. Aluminum-titanium alloy with high specular reflectivity, reflecting coatings comprising same and mirrors and parts comprising said coating. United States Patent US 6562471, 2003 May, 13.

[107] Huang LJ, Geng L, Wang B, Xu HY, Kaveendran B. Effects of extrusion and heat treatment on the microstructure and tensile properties of *in situ* TiBw/ Ti_6Al_4V composite with a network architecture. Compos Part A Appl Sci Manuf 2012; 43(3): 486-91.

[108] Cheng XL, Zhang H, Bai BZ, Fu HG, Guo L. Investigation on high temperature compression behaviour of hydrogenated Ti_6Al_4V alloy. Mater Sci Technol 2011; 27(10): 1547-50.

[109] Peirs J, Verleysen P, Degrieck J. Novel technique for static and dynamic shear testing of Ti_6Al_4V sheet. Exp Mech 2012; 52(7): 729-41.

[110] Reig L, Amigo V, Busquets DJ, Calero JA. Development of porous Ti_6Al_4V samples by microsphere sintering. J Mater Process Technol 2012; 212(1): 3-7.

[111] Tan Y, Chi YL, Huang YY, Yao TQ. Finite element simulation of extremely high speed machining of Ti_6Al_4V alloy. App Mech Mater-Functional Manuf Mech Dyn II 2011; 141: 293-97.

[112] Sekar KSV, Kumar MP. Finite element simulations of Ti_6Al_4V titanium alloy machining to assess material model parameters of the Johnson-Cook constitutive equation. J Braz Soc Mech Sci Eng 2011; 33(2): 203-11.

[113] Friderikos O, Korlos A, David C, Tsiafis I. Investigation of shear instability in orthogonal machining of Ti_6Al_4V alloy using the finite element method. 7th GRACM International Congress on Computational Mechanics: Athens, 30 June-2 July 2011: 40.

[114] Lei YW, Niu W. Prediction of Processing Parameters of Laser Clad TiC/NiCrBSiC Coatings on Ti_6Al_4V by Finite Element Analysis. Adv Mat Res-Manuf Process Technol 2011; 189-193: 1547-50.

[115] Peirs J, Verleysen P, Degrieck J. Experimental study of the high strain rate shear behaviour of Ti_6Al_4V. App Mech Mater-Performance, Protection and Strengthening of Structures under Extreme Loading 2011; 82: 130-5.

[116] Ratchev SM, Afazov SM, Becker AA, Liu S. Mathematical modelling and integration of micro-scale residual stresses into axisymmetric FE models of Ti_6Al_4V alloy in turning. CIRP J Manuf Sci Technol-Spec Sect Innov Cognt Manuf Eng 2011; 4(1): 80-9.

[117] Yang JH, Sun SJ, Brandt M, Yan WY. 3D finite element modeling of the machining of Ti_6Al_4V alloys. Adv Mat Res-Manuf Process Technol 2011; 189-193: 1926-9.

[118] Guo HF, Zhou JZ, Sun T, Li JL, Li Z. Finite element analysis for temperature field of laser remelting plasma sprayed Ni-based gradient coating on Ti_6Al_4V alloy surface. Adv Mat Res-Manuf Process Technol 2011; 189-193: 340-6.

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