

Development and use of titanium alloys for biomedical and orthopedic applications

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Abstract

Materials that can perform and mimic biological functions have been in high demand in the medical field since the invention of prosthetics. A variety of implant materials have been tested and applied to meet a wide variety of medical needs. In recent years titanium alloys and titanium-based alloys have been a focus for the use of biomedical and orthopedic applications due to their superior mechanical behavior and biocompatibility. Various attempts to improve on their properties have been made such as processing changes and surface modifications. This review summarizes the existing research that has been made to develop a more effective titanium alloy for biomedical and orthopedic applications.

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1. Introduction

Biomedical materials are materials that are manufactured and processed with the intent of being used for the development and creation of medical devices. These materials are often integrated into biological systems to fulfill the technical functions of the system while accommodating its biological interactions. To do this, good biocompatibility is a necessity. Biocompatibility is the ability of a material to perform its desired functions without causing any local or systemic adverse response in the recipient of the material. Instead the material in question should elicit the most appropriate and beneficial cellular and tissue response to optimize the clinical performance. Biocompatibility is a dynamic process as the properties of the material and the response of the host changes over time, some of these properties being corrosion resistance and aging [1].

For the orthopedic and dentistry applications of biomaterials metals and metal alloys are the preferred material. While widespread in their use metal alloys fall victim to corrosion and wear that can cause them to fail during their service. It has also been shown the mismatch of Young's modulus with the body parts and low strength can also increase the likelihood of failure with prosthetics resulting in

corrective surgery. These surgeries are expensive, painful and at times unsuccessful. Research to overcome the present issue plaguing implant materials has prompted the development of new titanium alloys to meet the desired criteria for an ideal biomaterial. In order to function in a biological environment, the developed alloy must be tough, corrosion and wear resistant, biocompatible, bioactive and be able to survive of long periods of time without failure [2].

2. Titanium Alloys

In recent years titanium and titanium-based alloys have become prominent for orthopedic implants. Originally used in the aerospace field, titanium alloys gained notable attention due to their biocompatibility, low modulus of elasticity, and corrosion resistance. Titanium implants are used to create prosthetic hips, knee replacements, and as fracture fixation devices such as plates, screws, and intramedullary rods. These alloys are expected to last about ten years or longer based on its usage. Unfortunately, this is not assured as the implant cannot always successfully integrate into bone leading to failure requiring revision surgery. It was not until the osseointegration phenomenon formed naturally on the oxide

later of a titanium surface that titanium alloys were heavily sought after for orthopedic applications [3].

Osseointegrative bioactivity is often not enough to maintain good adhesion between the implant and bone which can lead to mechanical instability and implant failure. For the development of a suitable titanium alloy the Young's modulus should be like that of cortical bone. The properties of titanium alloys vary depending on the composition as titanium, which has been used in both its α , β , and ($\alpha + \beta$) phases in biomedical applications. By adding alloying elements it is possible to give titanium an increased range of properties. These elements are characterized based on the type of stabilizing element that is added to the titanium; these groups are α stabilizers, β stabilizers, and neutral elements [4].

In studying the different compositions, manipulating the surface characteristics, and pairing multiple elements with titanium it was found that β -type titanium alloys contain a more suitable young's modulus than other compositions [5]. This discovery prompted the development of harmless low-rigidity alloys which have proven effective in preventing bone atrophy and enhancing bone remodeling. Their low fatigue strength makes them ineffective as a long-term implant material. Many researchers have been working to develop other grades of alloys using various compositions and alloying elements to create a high functioning and successful implant material [5].

3. Osseointegration of Titanium Alloys

In the hunt to create an all-encompassing titanium for implantology many new alloys have developed within the last decade. One of these many alloys is Ti-6Al-2Nb-2Ta-1Mo, which has a high potential as a biomedical implant material when compared to titanium and a Ti-6Al-7Nb alloy. Knowing that titanium shows viable osteointegration activity it is necessary to test the bone to implant surface attraction of its alloys. As a suitable attachment between the implant and its recipient is a critical first step in the success of the treatment. In an in vitro test done to monitor the corrosion resistance of the materials in a Hank's Balanced Salt Solution (HBSS), and in a in vivo test done to evaluate the osteointegration of the material following implantation into a rabbits tibia, an electrochemical impedance spectroscopy (EIS) analysis showed that the corrosion resistance of the Ti-6Al-2Nb-2Ta-1Mo was greater than that of the pure titanium and of the Ti-6Al-7Nb alloy.

The in vivo test also noted that a higher degree of osseointegration was achieved by the Ti-6Al-2Nb-2Ta-1Mo alloy, suggesting that a higher resistance to electrochemical corrosion could have provided an enhanced protection to the implant surface against biodegradation. This protection positively affected the evolution of the bone tissue repair. The in vivo study also worked to demonstrate the ability of titanium alloys containing Al and Nb to promote higher osteogenesis during the first month after implantation [6].

4. Corrosion Behavior of Titanium Alloys

The main limitation to titanium alloys in biomedicine is their high friction coefficient that causes severe adhesive wear. The properties of these varying alloys have also been seen to depend on the heat treatment to which the alloy has been subjected. Hydrogen peroxide is a component found within the body during inflammatory conditions, and as such it was used to simulate the inflammatory effects on corrosion resistance of a Ti-6Al-4V alloy submerged in Hank's physiological solution.

It was found that although hydrogen peroxide is a powerful oxidant that produces a thicker oxide layer onto the surface of the titanium alloy, adding hydrogen peroxide into Hanks' solution increased the films' instability. The addition of hydrogen peroxide into Hanks' solution decreased the polarization resistance of the Ti-6Al-4V alloy. The electrochemical results also demonstrated that the addition of hydrogen peroxide decreased the corrosion resistance of the alloy [7]. In another study done comparing the corrosion characteristics of Ti-6Al-4V and TMZF (Ti-12Mo-6Zr-2Fe) in a simulated body fluid, it was found that their corrosion corresponded to the combined differences in their elastic modulus and surface chemistry which is related to their electrochemical behavior [8].

5. Use of Surface Treatments to Promote Biocompatibility

Plasma electrolytic Oxidation (PEO) has been demonstrated to be an effective surface treatment for enhancing the osseointegration and osseointegration of commercially pure α -Ti implant materials. Thus, it has been posed that using PEO on low-modulus β -type titanium alloys could also increase its osseointegration. To test this theory a 10kW 50Hz KeroniteTM processing unit was used to modify the surface of low-modulus β -Ti13Nb13Zr and β -Ti45Nb before an in vitro culture of foetal human osteoblast (fHOb) cells was done on the substrates. The behavior of the cells on the β alloys was like that of pure α -Ti. This result demonstrated that it is possible to utilize PEO technology to modify the surface of low-modulus β -type titanium alloys with porous structure facilitating osseointegration. This can be done without impeding osteoblast activity or introducing an unwanted inflammatory response [9].

Titanium alloys are also known to form bio-inert thin films of oxides on metal surfaces. This film stops the alloys from being able to form a direct bone/material chemical interface, thus limiting the overall strength of its bonding. Additional research is needed to understand the various physical and chemical processes seen on the surface of a biocompatible implant. This information would allow for researchers to determine the adhesive strength between the bone and its surface. It was posed that it is possible to improve the inertness of the titanium oxide layer to behave like a bioactive surface using PEO that has electrolytes containing Mg and Si ions. Plasma electrolytic oxidation in other medical applications has been seen to produce a crystalline rutile/anatase film that is suitable for biocompatibility.

Coatings of functional elements such as Si, Mg, Ca, and P on Ti-alloys for biomaterials via PEO were studied using thin-film X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), and energy-dispersive X-ray spectroscopy (EDS). In using Ti-6Al-4V alloy to act as the substrate for the coating of PEO thin films it was noted that PEO treatment was suitable for creating an environment for cell proliferation. It was also shown that this treatment can improve the biocompatibility by allowing for doping when the PEO process is conducted in electrolytes containing calcium and phosphorous [10].

6. Effects of Thermochemical Treatments

The microstructure of a metal plays a critical role in the mechanical properties of implants. The α to β transus temperature effects the transformation of the microstructure in the case of titanium. This temperature dictates the types of heat treatments that the material requires. To test the effects of multiple thermochemical treatments on the crystalline structure, microstructure, hardness and elastic modulus of Ti-20Zr-Mo alloys Kuroda, et al. varied the concentrations of Molybdenum (Mo) within the alloy and subjected it to various degrees of hot rolling, homogenization, and annealing.

For the experiment five samples of Ti-20Zr-xMo were created with each weighing 60 grams. These samples were produced in an argon arc melting furnace with the molybdenum concentration varying in each. The variations of molybdenum included 0, 2.5, 5, 7.5, and 10 wt%. This variation was done as a response to molybdenum acting as a β stabilizing element. Adding molybdenum to titanium alloy has been noted to decrease the Young's modulus due to the formation of the β phase, however adding a high concentration of molybdenum to the sample has been suspected to impact the overall mechanical properties of the material. In the end it was demonstrated that hot rolling is the most effective thermochemical treatment method to decrease the Young's modulus value of the high Mo concentrated ternary Ti-20Zr-Mo samples, allowing it to meet the ideal mechanical and biocompatibility for biomedical and orthopedic applications. Alongside this it was seen that the addition of molybdenum did in fact impact the overall mechanical properties of the titanium alloy [11].

Thermally oxidized titanium alloys are used as biomaterials due to their better surface properties. However, the use of cyclic thermal treatment for this purpose has not yet been largely reported. Maestro, et al. aimed to compare roughness, microhardness, and corrosion resistance after cyclic and conventional isothermal heat treatments in a Ti6Al4V alloy. The samples used in the experiment were heat treated for a period of 24 hours reaching a maximum temperature of 650 °C. After various thermal treatments the roughness of the samples were recorded, and a Vickers hardness test was performed. In addition to this the corrosion resistance was tested in a simulated body fluid. In this experiment it was found that isothermal and cyclic treatments presented similar behaviors. The 650-200 °C cyclic heat treatment provided an intermediate roughness and produced a slightly better corrosion resistance, demonstrating that cyclic

thermal treatments are a viable alternative for improving titanium alloy surface properties [12].

Alloys based on the Ti-rich side of Ti-Nb-Sn systems have presented material properties that are functional and desirable for orthopedic applications. However, the structure and surface of these alloys has not been tested thoroughly. Rezende, et al, synthesized Ti-18Nb-11Sn and Ti-35Nb-4Sn alloys and tested the impact of thermochemical treatment on its bioactivity. The results produced indicated that the Ti-18Nb-11Sn alloy displayed a low hardness value making it unsuitable for biomedical application and was not demonstrated to be bioactive. In contrast to this the Ti-35Nb-4Sn alloy displayed a slight bioactivity that increased after thermochemical treatment while displaying an acceptable hardness value. This suggests that the Ti-35Nb-4Sn alloy may be attractive for designing biomedical devices with improved performances toward the adhesion of apatite [13].

7. Conclusion

There is a wide range in the chemical compositions, processing, and mechanical properties that come with titanium and its alloys. Since the 1960s titanium alloys have been used as implant materials and have managed to maintain its hold on the industry. Pure Titanium and Ti-6Al-4V are the most widely used implant material to date. Though the continued use of these materials is not without drawbacks. The Young's modulus of these materials is greater than that of bone while still being smaller than that of alternate metals. For this reason, β -Titanium implants such as the prospective Ti-29Nb-13Ta-4.6Zr alloy [14], are being developed and manipulated to meet the need for a Young's modulus equal, if not similar to that of bone to ensure a higher success rate in the bonding between the implant and its host.

Different thermochemical processing techniques have been used to alter the microstructure and resulting properties of titanium with additional alloying materials assisting in their biocompatibility. In a similar manner surface treatment such as PEO have been implemented to better the wear, corrosion resistance, and bonding of the titanium implants. Further processing techniques, surface treatments, and thermochemical studies are needed to create an all-encompassing titanium implant material. But once perfected a suitable titanium alloy could bring an end to the need for expensive and often painful revision surgeries that plague the biomedical field and those who need its prosthetic and implant services.

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Conflict of Interest

The authors have no conflict of interest.

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