Jurnal Rekayasa, Teknologi, dan Sains, Volume 7, No.1, Januari: 01-58

JURNAL REKAYASA, TEKNOLOGI, DAN SAINS
ISSN 2541-4720 (Print)
ISSN 2549-984X (Online)

INFORMASI ARTIKEL
Disubmit: 28 Desember 2022
Diterima: 26 Januari 2023
Diterbitkan: 31 Januari 2023
at : http://ejurnalmalahayati.ac.id/index.php/teknologi/index

Review on titanium-based alloys as biomaterials for implant applications

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ABSTRACT

Technological updates in the field of advanced materials research now tend to focus on biomedical materials application and utilization of Titanium and its alloys*. Various of implant materials have been employed in various disciplines of medical science depending on the requirements of a particular application. Metals, alloys, ceramics, and polymers are the commonly used biomaterials. Titanium and its alloys are commonly used in almost all disciplines of medicine because of their sufficient biocompatibility and meeting of mechanical requirements. The main focus of this study is to review the various structural and microstructural properties of titanium and titanium-based alloys used as orthopedic implants. Orthopedic implants need to possess certain important qualities to ensure their safe and effective use. These properties like the biocompatibility, relevant mechanical properties, high corrosion and wear resistance and osseointegration are summarized in this review. Various attempts to improve upon these properties like different processing routes, surface modifications have also been inculcated in the paper to provide an insight into the extent of research and benefit that has been put into developing a highly superior titanium orthopedic implant. In addition, this paper also discusses in detail the various surface modification techniques to achieve superior biocompatibility, higher wear and corrosion resistance. Overall, an attempt has been made to bring out the current scenario of Ti based materials for biomedical applications.*

Keywords*: titanium, implant, biomaterial.*

1. INTRODUCTION

Biomaterials mainly find use in orthopaedics, dental care, drug delivery, tissue engineering of skin and cardiovascular devices. Before recognising any material as an implant, it is imperative to know that the said material is not causing any damaging effect i.e., it should be biocompatible to the human body. This means that the implant should not release toxic substances in the body as these can cause systemic damage to the patient. Any material upon implantation in the human body triggers some kind of response. This response is more pronounced at the tissueimplant interface since the interface is more reactive than the core of the material. Basically, the interface is considered as a two-dimensional imperfection where the atoms are not linked to the highest number of neighbours. As a result, they possess higher energy than core atoms of the materials (Kaur & Singh, 2019). Biomaterials can be divided into four major classes: metals and their alloys, polymers, ceramics and natural materials. These are extensively being used in different medical fields: as cardiovascular biomaterials, for generation of skin substitutes, in drug delivery systems and in the treatment of cancer by hyperthermia. This is where biomaterials play a key role in bone repair and regeneration. Surgical implants made from biomaterials are used in restoring the function of an otherwise damaged part. Various types of implant materials are currently in use, these have varying properties. Amongst metals, 316L stainless steel, cobalt chromium alloys, and titanium-based alloys are the frontrunners in various orthopaedic applications like fracture fixation, hip joint replacement and dentistry (Geetha et al., 2009). The advancement in orthopaedic surgery has seen tremendous growth in the last few years as new and improved techniques for bone repair have been developed but still, there are some areas where work needs to be done. Sometimes the alloys fail in the long run owing to various reasons like corrosion, wear, mismatch of Young's modulus with the body parts and low strength. As a result, a second surgery becomes necessary. These revision surgeries are expensive, painful and at times are not even successful. New metallic alloys are being developed to overcome the issues of present implant materials. It is important to develop materials which are tough, corrosion and wear resistant, biocompatible, bioactive and can survive long periods of time without failure (Wally et al., 2015).

In most cases, they result from the failure of the treatment of the long bones. Especially, problematic are comminuted fractures of long bones with loss of bone tissue. In such cases, amputation of the limb is a frequent complication resulting in permanent disability. This generates significant social and economic costs. One of the main causes of disability are injuries of organs of motion. Many times, these types of injuries finally lead to pseudo joints and other results with permanent disability which, as mentioned before, lead to real measurable social and economic loss. In addition, the financial impact also concerns the relatives of these people because the participation of relatives in a physically disabled person's rehabilitation reduces their productive work time. In the last few decades, dental implants have become an integral part of the prosthetic rehabilitation of the oral cavity. Also, the number of implants being used is still growing and now, it is estimated to exceed one million implants per year. Osseointegration, which is a process that defines treatment success, is related to implant geometry and surface topography. These factors, in connection with the material, are responsible for the interaction of the implant with the body fluids, directly and indirectly stimulating bone on, and ingrowth. Proper, direct connection of the implant with bone is mandatory for rapid loading, as well as both short- and long-term functionality. Metallic biomaterials such as titanium, cobalt, stainless steel, tantalum, and magnesium (and alloys) have recently been used in a magnitude of load-bearing orthopedic devices (Balasubramanian et al., 2021). However, these materials may present several disadvantages, as in selected cases they exhibit insufficient osseointegration capacity and adverse reaction of the host tissues to the release of metallic ions. Last but not least, dense forms of such biomaterials misfit young's modulus causing stress-shielding, interfacial instability of the bone to implant contact. In consequence, leading to fibrous tissue ingrowth at implant interface, osseointegration disruption, implant mobility, and the development of an inflammatory response that leads to the necessity for revision surgery.

Thus, the implants are now expected to serve for much longer period or until lifetime without failure or revision surgery. Thus, development of appropriate material with high longevity and excellent biocompatibility is highly essential. While several materials are currently in use as biomaterials, titanium alloys are fast emerging as the first choice for majority of applications. This

DOI: https://doi.org/10.33024/jrets.v7i1.8762

paper presents an overview of various aspects of titanium alloys that make this material an ideal choice for bio-applications. The article is divided into ten sections, starting with the requirements to be fulfilled by biomaterials, the status of the current biomedical materials and their limitations, classification of titanium alloys, structure property correlations, effect of heat treatment on modulus, wear and corrosion properties of biomedical alloys and their remedies, surface modifications required for high resistance to wear and corrosion and enhanced osseointegration and biocompatibility issues of titanium alloys and future biomaterials (Bansiddhi et al., 2008).

2. MATERIALS AND METHODS

Metallic implants have been used for biomedical applications since the 19th century. Since then metallic implants have become an integral part of orthopaedic surgery. They are used as temporary as well as permanent implants in the body. Metals possess many properties which make them highly acceptable for bone repair. Tensile strength in case of metals is quite high better than polymers and noticeably higher than most bioceramics (the exception being zirconia). Metals are highly tough, 20 times higher than ceramics and possess a reasonable fatigue life. Metals have Young's modulus values quite close to those of ceramics. However, metallic corrosion can be a problem but if carefully selected, metals can show reasonable corrosion resistance (Balasubramanian et al., 2021; Rodriguez-Contreras et al., 2021; Stepanovska et al., 2020; W Nicholson, 2020). Metals show the ability to alloy which means their corrosion, wear, and mechanical properties can be altered and they can be made suitable for the required applications. Also, biocompatibility can be improved by using those elements which show no adverse effects in the body. Hence metals have proven to be quite useful for implantable device applications and this trend is not expected to change any time soon. Titanium is the ninth most abundant element on earth. In the 1950's titanium was developed for aerospace applications but after the 1960's it has been used in surgical implants. These days, 2% of titanium is used in medical applications. Titanium has become so popular because of its excellent combination of strength, Young's modulus and biocompatibility as compared to other metallic implant materials. The materials currently used for surgical implants include 316L stainless steel (316LSS), cobalt chromium (Co–Cr) alloys and titanium and its alloys. Elements such as Ni, Cr and Co are found to be released from the Stainless steel and cobalt chromium alloys due to the corrosion in the body environment. The toxic effects of metals viz., Ni, Co and Cr released from prosthetic implants have been reviewed by Wapner. Skin related diseases such as dermatitis due to Ni toxicity have been reported and numerous animal studies have shown carcinogenicity due to the presence of Co (Kaur & Singh, 2019; Pałka & Pokrowiecki, 2018; Wally et al., 2015).

In addition, both 316L SS and Cr–Co alloys possess much higher modulus than bone, leading to insufficient stress transfer to bone leading to bone resorption and loosening of implant after some years of implantation. The high cycle fatigue failure of hip implants is also reported as the implants are subjected to cycles of loading and unloading over many years. Amongst the materials available for implant applications, the natural selection of titanium-based materials for implantation, is due to the combination of its outstanding characteristics such as high strength, low density (high specific strength), high immunity to corrosion, complete inertness to body environment, enhanced biocompatibility, low modulus and high capacity to join with bone and other tissues Coming to Ti alloys, their lower modulus varying from 110 to 55 GPa compared to 316 L stainless steel (210 GPa) and chromium cobalt alloys (240 GPa), which have been used for the past several years is a very positive factor. Attempts to use titanium for implant fabrication dates back to the late 1930s when it was found that titanium was well tolerated in cat femurs, like other implant materials such as stainless steel and vitallium (a CoCrMo alloy). Commercially pure Ti and Ti–6Al–4V ELI (Ti64, Extra Low interstitial) are most commonly used titanium materials for implant applications. In spite of the fact that Ti64 was originally developed for aerospace applications, its high corrosion resistance and excellent biocompatibility led its entry into biomedical industry.

Apart from the implant applications titanium alloys are used in healthcare goods such as wheel chairs, artificial limbs, artificial legs etc owing to their excellent compatibility and non-allergic nature. The alloys such as Ti–4.2Fe–6.9Cr (TFC) and Ti–4Fe–6.7Cr–3Al (TFCA) are being evaluated for making wheel chair frame as the weight of the chair made out of these alloys is calculated to be just 50% of pure titanium. The strength of the titanium alloys is very close to that of 316 L SS, and its density is 55% less than steel, hence, when compared by specific strength (strength per density), the titanium alloys outperform any other implant material. The range of application of

DOI: https://doi.org/10.33024/jrets.v7i1.8762

titanium and its alloys in medical area is truly astonishing. The applications cover dental implants and parts for orthodontic surgery, joint replacement parts for hip, knee, shoulder, spine, elbow and wrist, bone fixation materials like nails, screws, nuts and plates, housing device for the pacemakers and artificial heart valves, surgical instruments and components in high-speed blood centrifuges. Although titanium and its alloys mainly Ti64 have an excellent reputation for corrosion resistance and biocompatibility, long-term performance of these alloys has raised some concerns due to release of aluminum and vanadium from Ti64 alloy. Both Al and V ions released from the Ti64 alloy are found to be associated with long-term health problems, such as Alzheimer disease, neuropathy and ostemomalacia (Bansiddhi et al., 2008; Geetha et al., 2009; Sidambe, 2014).

3. RESULTS AND DISCUSSION

The interfacial zone between the titanium alloy implant and living bone is critical in the development of osseointegration. This region, which is thin (20–50 nm), is the region into which growth factors are released from the bone cells, and this initiates the steps that result in bone formation. The initial step is deposition of proteins from the blood plasma onto the surface oxide layer. This is followed by the formation of a fibrin matrix, a structure that acts as a scaffold for osteoblasts (the bone-forming cells). Supported in this way, the osteoblasts lay down bone, which expands to fill the interfacial region, so that it grows right up against the implant surface, causing the implant to become osseointegrated. The important effect of proper osseointegration is that the implant is held rigidly, unlike the case where fibrous capsule forms, and in dentistry this provides a firm anchor for the prosthetic device. The oxide layer on the surface plays a major role in the success of osseointegration. Thicker and rougher oxide coatings encourage osseointegration to occur reliably and quickly, at least over the shorter term. The oxide coating also has the effect of passivating the metal, so that corrosion is inhibited and the release of titanium ions is minimized (Kaur & Singh, 2019; Rodriguez-Contreras et al., 2021; Sidambe, 2014).

Cells of various types interact with the surfaces of titanium alloys. These alloys have surfaces with the appropriate surface energy and charge, and the first thing they do is to attract a layer of proteins. A sequence of proteins is deposited, eventually leading to the deposition of extracellular matrix proteins and these stimulate the osteoblasts, which then become attached. As has already been mentioned, cells prefer rough, porous surfaces with an irregular morphology, of the type that can be readily produced on implantable devices. When dental implants are used, titanium levels in the blood and the serum are raised. The increases are minor but significant, and indicate that titanium is leached from these devices. Entering the blood stream indicates that the titanium released is capable of being transported round the whole body. However, in most patients, it has no toxic effects on any of the body’s tissues. In a very small number, there may be adverse systemic effects in the form of type IV reactions. However, these are very rare and affect only a very small number of patients. In most patients, titanium is completely acceptable within the body and its presence causes no adverse effects (Bansiddhi et al., 2008; Pałka & Pokrowiecki, 2018; W Nicholson, 2020).

4. CONCLUSION

The principal alloys in practical use are commercially pure titanium and Ti-6Al-4V. The mechanical properties of the latter are better, but the slight concern over the biological effects of the very minor amounts of aluminium and vanadium that they release means that cpTi is the more widely used of the two. Despite these concerns, there is a large amount of experimental evidence to show that both alloys have good bioactivity and the ability to osseointegrate. Additionally, there are few, if any, accounts of adverse effects arising from release of aluminium and/or vanadium from dental implants, probably because amounts released are so low. The result of the excellent biological and mechanical properties of titanium alloys is that success rates with dental implants made of these materials are very high. Various studies are described which show that failure rates over considerable time periods are extremely low. Depending on the details of the study and the materials used, at least 89% and typically 97–99% of implants survive for over 10 years. Given these results, the scope for improving either the materials or the clinical procedures is limited. For this reason, the two well-established alloys of titanium continue to be used for the

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overwhelming majority of implants used in dentistry, and this use seems likely to continue for the foreseeable future. Titanium and its alloy Ti64 used since 1950s as implant biomaterial, are being continuously subjected to various modifications with respect to alloy composition and surface properties in order to meet the need for improved function and duration of an implant in the human body. Development of an appropriate microstructure with optimum mechanical properties is a challenging problem in the field of b titanium alloys. Hence, more studies on the effect of thermomechanical processing on the properties of these alloys are required to gain a better understanding. Secondly, though the modulus of Ti alloys is far less than the conventional alloys like Stainless steel and chromium cobalt, intense research are still being pursued in the development of new titanium alloys with modulus closer to bone. At present Ti–35Nb–% 7Zr–5Ta possesses the lowest modulus of 55 Gpa. In spite of the fact the newly developed titanium alloys have modulus closer to bone and consist of highly compatible alloying elements, their wear resistance under loading conditions is very poor. Extensive research is presently being carried out to improve the wear resistance of Ti-based materials. However, due to the lack of appropriate protocol for measurements of wear property of metallic biomedical materials at present, only comparative studies are carried out at different conditions of loading and environment.

More research on development of an appropriate protocol for measuring the wear property should be performed for development of an alloy with better wear resistance. The performance of titanium and its alloys can be enhanced profoundly by developing an appropriate surface treatment procedure that will lead to increased wear resistance and osseointegration. Hence, it is suggested that in future, greater focus should be made on the areas of development of very hard nano surface of appropriate hardness on frictional parts and the formation of biomimetic surface in order to attain increased functional longevity of the implant in the human body. CP- Ti and Ti-6Al-4V (ELI) are the most widely applied implants but both of these have certain drawbacks. The Young's modulus of these

implants is certainly less than that of stainless steel and cobalt based alloys but it is still greater than that of bone. Today β titanium implants have been developed with the aim of decreasing the Young's modulus and improving the fatigue strength. Although the value of Young's modulus for β alloy is smaller than of its predecessor's still it is not close enough to the Young's modulus of bone. Materials with very low value of Young's modulus have been developed (~55 GPa) but they possess low wear resistance. Different thermomechanical processing techniques have been used to alter the microstructure and eventually the mechanical properties of the titanium implants. Further porous implants have received special attention as they help reduce Young's modulus and improve bone ingrowth. Alloying elements like aluminium and vanadium, widely used in various titanium implants are considered potentially dangerous. To a great extent these implants have proven their biocompatibility but still there have been few cases where allergy could have been caused due to the release of dangerous ions into the blood. As a result, efforts are being put into producing implants which display better biocompatibility. Also, different surface treatments are being used to improve the properties like wear and corrosion resistance and bone bonding in case of titanium implants. Different advanced processing techniques followed by proper surfacecoatings and modifications are being used to achieve the required properties of titanium implants however, more resources and research is needed to turn the dream of developing an implant material which is tough, biocompatible, corrosion and wear resistant and has the value of Young's modulus closer to that of bone, into reality.

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