EFFECT OF THERMAL OXIDATION ON CORROSION RESISTANCE OF Ti-8Mo-4Nb-2Zr ALLOY FOR BIOMEDICAL APPLICATION

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SULTAN IDRIS EDUCATION UNIVERSITY

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ABSTRACT

Titanium and titanium alloys are widely used in a variety of engineering applications. Medical device manufacturers have also benefited from the outstanding properties of titanium alloys. However, titanium alloys are weak in meeting all of the clinical requirements for biomedical implants. Issues such as metal sensitivity associated with high levels of metal ion release triggered by corrosion effects remain critical concerns. Hence, the implant material surface has a strong role in the responses to the biological environment the implant can be stimulated in contact with the bone. In order to improve the biological and tribological properties of implant materials, surface modification needed to be made. Thermal oxidation is one of the surface modification techniques to enhance the corrosion performance of titanium alloys. This technique is excellent for forming a thicker oxide layer on Ti and its alloys to achieve optimum corrosion resistance. In the present study, thermal oxidation of Ti-8Mo-4Nb-2Zr alloy was explored. Hence, experiments were carried out to investigate the effective combination of surface modification parameters and evaluate performance corrosion behaviour in terms of their suitability with the Ti-8Mo-4Nb-2Zr alloy surface for biomedical implants applications. Process thermal oxidation was carried out at 500, 600 and 700°C for three different durations of 6, 12 and 24 hours. It was found that particles of oxides formed were noticeably larger after oxidation at an increased temperature of 600°C and 700°C. The increase in temperature resulted in the formation of compact particles in the oxide layer. A phase analysis showed that the phase contents of the oxide layer showed a strong dependence on treatment conditions with a predominance of the rutile phase over the anatase phase at temperatures > 500°C and for time periods > 6h. Improved corrosion resistance had been achieved of these alloys using thermal oxidation. EIS was employed to measure the corrosion resistance of the Ti-8Mo-4Nb-2Zr alloys in simulated physiological solutions of a wide pH range (namely 7.4 pH) at 37°C, and the best results were obtained for the alloys at 700°C. A more positive Ecorr value (-0.125 V) and a lower Icorr value (2.583 A x 10-6) were observed for the thermally oxidized Ti-8Mo-4Nb-2Zr alloys when compared with the untreated alloy. This finding, the oxide scale on the examined alloy efficiently enhances can increase the corrosion resistance of the implant material.

KESAN TERMA OKSIDA TERHADAP KETAHANAN KAKISAN PADA ALOI Ti-8Mo-4Nb-2Zr UNTUK KEGUNAAN BIOMEDIK

ABSTRAK

Titanium dan aloi titanium digunakan secara meluas dalam pelbagai aplikasi kejuruteraan. Pengilang alat perubatan juga mendapat manfaat daripada sifat aloi titanium yang luar biasa. Walau bagaimanapun, aloi titanium lemah dalam memenuhi semua keperluan klinikal untuk implan bioperubatan. Isu seperti kepekaan logam yang berkaitan dengan tahap pelepasan ion logam yang tinggi yang dicetuskan oleh kesan kakisan tetap menjadi perhatian kritikal. Oleh itu, permukaan bahan implan mempunyai peranan yang kuat dalam tindak balas terhadap persekitaran biologi implan dapat dirangsang bersentuhan dengan tulang. Untuk meningkatkan sifat biologi dan tribologi bahan implan, perlu dilakukan pengubahsuaian permukaan. Pengoksidaan termal adalah salah satu teknik pengubahsuaian permukaan untuk meningkatkan prestasi kakisan aloi titanium. Teknik ini sangat baik untuk membentuk lapisan oksida yang lebih tebal pada Ti dan aloi untuk mencapai ketahanan kakisan yang optimum. Dalam kajian ini, pengoksidaan termal aloi Ti-8Mo-4Nb-2Zr telah diterokai. Oleh itu, eksperimen dijalankan untuk menyiasat kombinasi parameter modifikasi permukaan yang berkesan dan menilai tingkah laku kakisan prestasi dari segi kesesuaiannya dengan permukaan aloi Ti-8Mo-4Nb-2Zr untuk aplikasi implan bioperubatan. Proses pengoksidaan termal dilakukan pada suhu 500, 600 dan 700°C selama tiga jangka masa berbeza iaitu 6, 12 dan 24 jam. Didapati bahawa zarah-zarah oksida yang terbentuk kelihatan lebih besar setelah pengoksidaan pada peningkatan suhu 600°C dan 700°C. Peningkatan suhu mengakibatkan pembentukan zarah padat di lapisan oksida. Analisis fasa menunjukkan bahawa kandungan fasa lapisan oksida menunjukkan pergantungan yang kuat pada keadaan rawatan dengan dominasi fasa rutil terhadap fasa anatase pada suhu > 500° C dan untuk jangka masa > 6 jam. Rintangan kakisan yang lebih baik telah dicapai pada aloi ini menggunakan pengoksidaan termal. EIS digunakan untuk mengukur ketahanan kakisan aloi Ti-8Mo-4Nb-2Zr dalam penyelesaian fisiologi simulasi dengan julat pH yang luas (iaitu 7,4 pH) pada 37°C, dan hasil terbaik diperoleh untuk aloi pada suhu 700°C. Nilai Ecorr yang lebih positif (-0.125 V) dan nilai Icorr yang lebih rendah (2.583 A x 10-6) diperhatikan bagi aloi Ti-8Mo-4Nb-2Zr yang teroksida termal jika dibandingkan dengan aloi yang tidak dirawat. Penemuan ini, skala oksida pada aloi yang diperiksa dengan cekap dapat meningkatkan daya tahan kakisan bahan implan.

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LIST OF SYMBOLS

Α	Alfa
β	Beta
ºC	Celcius
Gpa	Giga Pascal
h	Hour
m	Milli
nm	Nano milli
µm	Micro milli
V	Voltan
KeV	Kiloelectron Volt
Co-Cr	Cobalt Chromium
Ti	Titanium
Mo	Molybdenum
Nb	Niobium
Zr	Zicronium
Cp	Commercial Pure
Ta	Tantalum
Al	Aluminium
V	Vanadium
O	Oxygen
C	Carbon
N	Nitrogen
Mg	Magnesium
Fe	Iron
Sn	Tin
Zn	Zinc
F	Fluorine

CI	Chlorine
Br	Bromine
Hf	Hafnium
W	Tungsten
CVD	Chemical Vapour Deposition
EDX	Energy Dispersive
MAO	Micro-arc Oxidation
PVD	Physical Vapour Deposition
SEM	Scanning Electron Microscope
XRD	X-ray Diffraction
EIS	electrochemical impedance spectroscopy
Ecorr	Corrosion Potential
Icorr	Coorosion Current

CHAPTER 1

INTRODUCTION

1.1 Background of the research

In the technological age now, there is a need for the development of biomaterials with novel properties in biomedical purposes (Konovalova et al., 2017). It also reported the development and characterisation of new metallic biomaterials that contain non-toxic and non-allergic elements has become a topic of serious investigation in orthopaedic implant application (Nnamchi, Obayi, Todd & Rainforth, 2016). Therefore, field of biomaterial has caught the attention of researchers because it can increase the length and quality of human life. From the research viewpoint, biomaterial is an increasingly important topic, calling for a good mastery of knowledge in materials, biology, physics, chemistry (Li et al., 2014). Natural and artificial biomaterial is used to make implants or structures that replace biological structures lost to diseases or accidents. The application of biomaterial in musculoskeletal implants include dental implants, artificial hips, and knees prostheses and incorporate the screw, plates, and nails in these devices. The material used in surgical implant include stainless steel (316LSS), Co-Cr based alloys and Ti alloys. Titanium based alloys are preferable due to their excellent biocompatibility, outstanding corrosion resistance, relatively good fatigue resistance and lower elastic modulus (Zhang, Wang, Li & Zheng, 2010).

Commercially pure titanium (Cp-Ti) and its alloys have been widely used in chemical, nuclear, aerospace, and biomedical applications due to their low density, excellent corrosion resistance, biocompatibility, and mechanical properties. Lately, the research on biomaterials has gathered significant interest as these materials are extensively used to fix and replace decayed or damaged parts of the human systems such as heart valves, bones, joints and teeth, etc. (Mohammed, Khan & Siddiquee, 2014). Kumar, Narayanan, Raman and Seshadri (2009) reported the widespread use of Ti and its alloys as bio-implant materials, particularly for orthopaedic and osteosynthesis applications, due to their exceptionally sought properties mentioned above.

The literature reveals that surface properties and biocompatibility have major roles in the response of biomaterial. Biomaterials have been defined as any substance (other than a drug) or combination of substances, synthetic or natural in origin, which can be used for any period of time, as a whole or as a part of a system which treats, augments, or replaces any tissue, organ, or function of the body (Boretos & Eden, 1984). Hence, in order to enhance the performance of biomaterial within the biological system, a crucial need arises to optimize its surface. In addition, the biocompatibility of the material is important and needless to say it must be non-toxic and should not cause any allergic reaction with the human body.

However, titanium alloy has a drawback such as high corrosion rate, especially when coming in contact with body fluid. It is well understood that the body environment is very aggressive owing to the presence of chloride ions and proteins. The corrosion of implant releases toxic ions to the host body and causes inflammation which in some cases requires revision of surgery (Geetha, Singh, Asokamani & Gogia, 2009). Ti6Al4V has been extensively used for implant manufacture, but concerns have been raised about their long-term effects because of their vanadium and aluminium content (Manjaiah& Laubscher, 2017)

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This issue can be addressed to a large extent by a suitable surface coating or surface modification techniques. Common surface treatment techniques include Chemical Vapor Deposition (CVD) (Bensheng, Ge, Zhongying, Wenfeng & Qi, 2015), Physical Vapour Deposition (PVD) (Rahmati et al., 2016), Ion Implantation (Sun, Xue, Liu, Wang & He, 2015) and Plasma Spray coating. Among them, thermal oxidation is the simplest and economical method for enhancing the corrosion resistance of titanium alloy. During the thermal oxidation process, titanium can easily react with air and produce oxides either with rutile, brookite or anatase structure due to its affinity to oxygen. Surface characteristics of certain metals, such as Ti and its alloys, can be enhanced via thermal oxidation treatment (Izman et al., 2012). During the thermal oxidation process, titanium can easily react with air and produce oxides either with rutile, brookite or anatase structure due to its affinity to oxygen. Among the three, rutile structure is preferable for several reasons. Rutile structure is more inert to bacterial attack and corrosion resistance (Bloyce, Qi, Dong & Bell, 1998), high hardness and low friction coefficient that can reduce wear as compared to other two structure (Krishna & Sun, 2005). Studies of effect the producing rutile structure on ANSI 3I6L coated with titanium (Krishna & Sun, 2005). They found that the presence of rutile structure improves the hardness and corrosion resistance. It can be concluded that several studies have carried out for thermal oxidation on various titanium alloy but the effect of thermal oxidation on Ti-8Mo-4Zr-2Nb have never been published yet. It was reported that the different element presence on the material can give significant effect on the behaviour of thermal oxidation.

1.2 Problem statement

Thermal oxidation techniques is one of the alternatives that can be used as surface treatment to improve the properties of titanium and its alloys, properties of the material surface layer (Sun, Hu, Fan, Zhang & Hu, 2016) also to combat corrosion and enhance the life span of the implant (Aniołek, Kupka & Barylsk, 2016). This techniques constitute either one methods is a relatively simple, cost effective, and economical (Aniołek, Kupka, Barylski & Dercz, 2015; Wen, Wen, Hodgson & Li, 2014). Thus, thermal oxidation treatment aimed to obtain a ceramic coating mainly focused on rutile structure is preferable due to its bioactivities properties such as cell growth, stress shielding, antibacterial effects and corrosion resistance. The many researchers reported that the thermally formed oxide layer enables an increase in hardness, wear resistance and corrosion resistance of titanium and its alloy (Aniołek, Barylski & Kupka, 2018; Aniołek et al., 2016; Huang, Wu, Sun & Lee, 2013; Wen et al., 2014). Additionally, substantial corrosion resistance is also very important for biomedical materials. If the materials with inferior corrosion resistance are implanted in the body, early failure and adverse effects on human health are likely to occur. Oliveira and Guastaldi (2008; Chui, Jing, Zhang, Li and Feng (2020) did not observe pitting corrosion in the potential scans in Ringer solution, suggesting a high corrosion resistance for the Ti-Mo alloys (Nnamchi et al., 2016).

Therefore, still now literature limited on systemic thermal oxidation behaviour of new titanium alloy Ti-Mo-Zr-Nb which focuses on rutile structure formation. But lately, the development of new titanium alloys for biomedical applications has was done on type β alloys, this is due to their smaller modulus of elasticity, which can be reduces the stress shielding effect (Nnamchi et al., 2016; Correa, Kuroda & Grandini, 2014). Element Molybdenum is a strong β-modulus of elasticity and better corrosion resistance (Zhou & Luo, 2011). Therefore, a systematic method of analysing thermal oxidation behaviour with rutile structure formation on this alloy is still worth to be investigated for enhancing bioactivity properties. Thus, it is hoped that research will help to reduce the cost of medical devices especially in producing the implant for orthopaedic application. This research can be use thermal oxidation technique on new titanium Ti-8Mo-4Zr-2Nb and the corrosion performance of thermal oxidation will be evaluated in a simulated body fluid by electrochemical methods.

1.3 Objectives of the research

The objectives of the research are:

i) To develop the titanium oxide layer of thermal oxidation process on titanium alloys.
ii) To analyze the effect of thermal oxidation temperature and time on surface morphology and structure.
iii) To evaluate the performance of corrosion resistance on coated and uncoated sample in body fluids.

1.4 Scopes of the research

The study was conducted using the following limits:

i) Ti-8Mo-4Nb-2Zr was used as the substrate material.
ii) Thermal oxidation technique was conducted in muffle furnace.
iii) Investigations of thermal oxidation carried out at three different temperature 500ºC, 600ºC and 700ºC and duration time 6h, 12h and 24h.
iv) Investigation of surface morphology carried out using the SEM, element analysis using the EDAX whiles the compound analysis using XRD.

1.5 Significance of the research

Development this research is expected to minimize the release of toxic ion into human body after implantation. Any improvement on the surface morphology of implant material can potentially increase the quality of biological response to human cell. This will boost up the healing capability of patient as well as resulting shorter post-surgery recovery time. In the long run, this research leads to produce bioactive implant manufacturing as well as reduce medical and surgical expenses. In addition, this research will open opportunities of producing homogenous rutile structure on biomedical implant made of Ti-8Mo-4Zr-2Nb. Massive presence of rutile structure on the treated implant surface able to enhance cell growth. This research will also contribute to produce implants and provides better corrosion resistance capability and finally enhances the whole implant life cycle. This will benefit large amount to of orthopedics patient as well as industries to compete with growing demands.