A Review on Wear and Corrosion Behavior of Thermal Oxidation on Titanium-based Alloy for Biomedical Application

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ABSTRACT

The surface modification technique has been reckoned as a potential approach in addressing and improving several properties in materials, such as chemical and phase compositions, thickness, morphology, and structure. Thermal oxidation treatment in air is a modification technique that has been widely applied, mainly because it is low in cost and it can easily enhance the properties by influencing both the structure and the properties of the material surface layer. As such, this paper looked into the technique of thermal oxidation treatment to enhance the aspects of wear and corrosion resistance against titanium-based alloy (Ti-based alloy) for biomedical application, such as for surgical implants. Ti and its alloys appear to be the most suitable materials for implants due to their low wear and corrosion resistance characteristics in body fluid, thus resulting in the release of non-compatible metal ions by the implants into the human body. Hence, treatment parameters should be weighed in and adjusted to attain optimum microstructure towards improving the surface characteristics of Ti alloys.

Keywords:
Thermal oxidation; wear; corrosion behaviour; biomedical implant

1. Introduction

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. [1]. Kumar, Narayanan, Raman, and Seshadri [2] 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.

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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 [3]. Hence, in order to enhance the performance of biomaterial within the biological system, a crucial need arises to optimise 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. 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 [4]. Surface characteristics of certain metals, such as Ti and its alloys, can be enhanced via thermal oxidation treatment [5]. The development of crystalline oxide film is promoted through oxidation typically at temperature exceeding 200 °C. A thick oxide layer is formed due to high temperature, which is accompanied with oxygen beneath it [6, 7]. This does not only prevent scaling or surface hardening, but also effectively hardens Ti alloys via thermal oxidation process. The benefits offered by thermal oxidation process can be ascribed to both the formation of thin oxide layer and oxygen diffusion zone [8]. Surface modification enhances substrates; energy, adhesion, biocompatibility, corrosion resistance, degradation, and most importantly, its tribological characteristics such as high corrosion and wear resistance, osseointegration, ductility and high hardness [9]. Hence, surface engineering plays a significant role in the improvement of the implantation process. While, researcher Siva Rama Krishna and Sun [10] had produced rutile structure on stainless steel coated with Ti. The studies discovered that the presence of rutile structure enhanced both aspects of hardness and corrosion resistance. With that, this paper discusses the effect of thermal oxidation on Ti-based alloy, particularly upon corrosion behaviour and wear.

2. Thermal Oxidation

Thermal oxidation treatments are typically aimed to obtain in-situ ceramic coatings, mainly based on rutile, which offers thick and highly crystalline oxide films, along with dissolution of oxygen beneath them. This method has been thoroughly investigated on numerous biomaterials with the primary focus of enhancing hardness and wear resistance [11]. The literature reveals that the surface modified by relatively simple thermal oxidation technique demonstrates superior properties over the others due to several reasons; easy, low in cost, and the ability to generate thick and highly crystalline rutile oxide film [12]. Prior studies have emphasised the absence of investigation involving thermal oxidation treatments on Ti alloys and agreed that treatment parameters should be optimised in order to gain optimum microstructure so as to improve the surface characteristics of Ti alloys by thickening the native oxide fill [13, 14]. Thermal oxidation temperature and time seem to be the leading factors to affect the performance of oxidised layer, surface roughness, cooling mode, etc. Nevertheless, high temperatures and prolonged durations can result in debonding stratification between the scales and the interface, while insufficient temperatures and durations may generate discontinuous oxides [15]. Therefore, thermal oxidation with optimum oxidation and time may enhance the corrosion resistance and wear behaviour. This simple method can improve implant biomaterial, particularly Ti-based alloy, due to the formation of rutile structure that is absent in other biomaterials, such as Cobalt-based alloy and stainless steel.
Table 1
Thermal Oxidation on various Material for Biomedical

<table>
<thead>
<tr>
<th>No.</th>
<th>Material</th>
<th>Range of temperature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>ZrTi</td>
<td>500°C</td>
<td>[16]</td>
</tr>
<tr>
<td>2.</td>
<td>Cp-Ti &amp; Ti6Al4V</td>
<td>400°C - 600°C</td>
<td>[17]</td>
</tr>
<tr>
<td>3.</td>
<td>Co-Cr-Mo Alloy</td>
<td>1050°C</td>
<td>[18]</td>
</tr>
<tr>
<td>4.</td>
<td>Titanium Grade 2</td>
<td>600°C and 700°C</td>
<td>[19]</td>
</tr>
<tr>
<td>5.</td>
<td>Titanium Alloy</td>
<td>700°C – 800°C</td>
<td>[20]</td>
</tr>
<tr>
<td>6.</td>
<td>Ti-6Al-4V alloy</td>
<td>400°C – 600°C</td>
<td>[21]</td>
</tr>
<tr>
<td>7.</td>
<td>Zr–xTi alloys</td>
<td>500°C</td>
<td>[22]</td>
</tr>
<tr>
<td>8.</td>
<td>Ti–6Al–4V alloy</td>
<td>1173 K</td>
<td>[23]</td>
</tr>
<tr>
<td>9.</td>
<td>Ti6Al4V alloy</td>
<td>500°C</td>
<td>[24]</td>
</tr>
<tr>
<td>10.</td>
<td>Mg alloys</td>
<td>300°C</td>
<td>[25]</td>
</tr>
<tr>
<td>11.</td>
<td>Ti6Al4V</td>
<td>400°C – 700°C</td>
<td>[26]</td>
</tr>
<tr>
<td>12.</td>
<td>Ti-6Al-7Nb alloy</td>
<td>600°C – 800°C</td>
<td>[27]</td>
</tr>
<tr>
<td>13.</td>
<td>Co-Cr-Mo</td>
<td>1160°C</td>
<td>[28]</td>
</tr>
</tbody>
</table>

2.3 Issues Regarding Thermal Oxidation on Titanium

2.3.1 Wear behaviour

Wear behaviour is defined as the damages found on solid surface that involve progressive loss of material due to relative motion [5]. The recent development of biometallic implant materials has highlighted the importance of avoiding stress transmission between hard tissue and biometallic components [29], mainly because the vast variances in rigidity, mechanical, and tribo-characteristics between bone and biometallic implant materials can accelerate bone loss and degradation. Fretting and sliding wear conditions lead to damages that can fracture the passive oxide film [30], which could be disrupted at very low shear stresses [31]. Nonetheless, Ti is an extremely reactive metal with poor tribo-characteristics [32] and inferior performance, in comparison to other implantable materials, such as Cobalt-Chromium alloys.

Degradation stems from wear and corrosion failures [33], as well as the massive difference in tribo-characteristics between bone and implant, which must be addressed to increase the service life of surgical implants, besides preventing bone degradation and adsorption [34]. The poor tribo-characteristics of Ti alloys are attributable to their low resistance to plastic shearing and low mechanical stability of the passive surface oxide layer, which appear to be crucial clinical issues [35] that may lead to premature removal of prostheses. Due to the tendency of Ti to gall and seize, a piece of bone may rub against the implant, or two parts of a total joint replacement rub against one another. The friction localises stresses at the contact regions and causes heavy damages on the surfaces that gradually consume the Ti material [35, 36] and thereby, generating wear debris that is often found at the implant surrounding tissues.

Thus, it is essential to address surface friction and to improve wear resistance of orthopaedic Ti alloys inside the human body to increase the longevity of total joint components. Endless research efforts have been devoted to study and to improve the performance of wear behaviour in biomedical Ti alloys. Various surface modification methods, such as ion implantation, TiN coating, thermal oxidation, composition adjustment, as well as selection of appropriate thermal and thermomechanical processing procedures, have been proposed to enhance wear resistance by enhancing its surface.

The techniques have been applied especially on the oxidation of pure Ti and Ti-6Al-4V alloy [37]. Nonetheless, the wear resistance of such alloys has remained a major obstacle to be employed in broader applications, where tribological effects are a major concern. Thermal oxidation treatment
for Ti–6Al–4V was performed by Güleryüz and Çimenoğlu [6] to study the optimum oxidation conditions in examining corrosion wear performance. This was determined based on the outputs of accelerated corrosion tests made in 5 m HCl solution. The examined Ti–6Al–4V alloy exhibited excellent resistance against corrosion after oxidation was performed at 600 °C for 60 h. The results revealed that the oxidation condition gave 25 times higher wear resistance than the untreated alloy during reciprocating wear test conducted in 0.9% NaCl solution.

Krzysztof Aniołek, Kupka, and Barylski [38] studied oxidation of Grade 2 Ti process at 600 °C and 700 °C for over 72 h. The tribological tests were conducted on a commercial ball-on-disc wear tester under conditions of technically dry friction with a 10 N load. The friction distance was 1000 m and an aluminium oxide (Al$_2$O$_3$) ball was used as the counter-specimen. The presence of oxide layer on the surface of Ti significantly increased the resistance to sliding wear. After oxidation of Ti disc at 600 °C and 700 °C, its volumetric wear decreased by 47 and 61%, respectively.

Hacisalioglu, Yildiz, Alsaran, and Purcek [39] compared Ti–15Mo and Ti–6Al–4V alloys in terms of wear performance to obtain alloys with similar microstructure in solution treated at 800°C and then air-cooled. Both plasma and thermal oxidations were applied at 650°C for 1 hour. As a result, Ti–15Mo alloy exhibited higher wear resistance, when compared to Ti–6Al–4V alloy under all conditions. Wear resistance of both Ti–15Mo and Ti–6Al–4V alloys oxidised by plasma appeared to be higher than those oxidised thermally.

Dearnley, Dahm, and Çimenoğlu [40] assessed the corrosion–wear behaviour of untreated and thermally oxidised CP–Ti and Ti–6Al–4V alloy. The thermal oxidation treatment of alloys at 625 °C for 36 h resulted in the formation of an exterior layer of TiO$_2$ (rutile) with hardness $\sim$1000 HV. Corrosion–wear tests were performed in reciprocation sliding contact with an Al$_2$O$_3$ ball immersed in physiological saline (0.89% NaCl) at room temperature. The behaviour wear of the oxidised materials was slower but more complex. The exterior TiO$_2$ layer formed on the oxidised Ti–6Al–4V alloy offered little protection, as it was rapidly removed during the first 60 min of testing through a process that involved interfacial fracture. On the contrary, the TiO$_2$ layer, albeit thinner, provided protection for the oxidised CP–Ti.

### 2.3.2 Corrosion resistance

Ti and its alloys are the most suitable materials for biomedical applications due to their well-established corrosion resistance and biocompatibility. They owe their excellent corrosion resistance to passive oxide film formation at room temperature [6]. Thus, oxygen can be introduced onto the surface of Ti using various methods, such as thermal or anodic oxidation and oxygen ion implantation, to improve its properties [41]. This passive film is typically a few nanometres thick and may be easily damaged. There is evidence that early bone response to electro-polished Ti, with a thinner oxide layer, displayed less bone volume and bone-to-implant contact [42]. Hence, this passive film, which mainly consists of TiO$_2$, was formed on Ti surface upon exposure to air or oxygen and also when dipped in many aqueous solutions. However, in their native form, TiO$_2$ films exerted poor mechanical properties and were easily fractured under fretting and sliding wear conditions. Sustained dissolution of underlying metal after disruption of oxide film and reformation of passive oxide layer resulted in gradual consumption of the material [36]. Besides, formation of wear debris and release of metal ions caused adverse tissue reactions, implant loosening, and eventually, revision surgery [6]. However, the material will not fail directly due to corrosion, as it was found to fail due to accelerated processes, such as wear and fretting, which led to tribo-corrosion. Fretting ruptured the protective oxide layer, initiated cracks, and formed reactive metal atoms on surfaces susceptible to corrosion [43].
Aniołek et al., [44] found that thermal oxidation process in air may be a method that can improve the properties of Ti and its alloys through its influence on the structure and the properties of the material surface layer. Thermal oxidation ensured the acquisition of a uniformly rough Ti surface and increment in surface energy. In short, the higher the oxidation temperature, the greater the scale surface roughness [38]. The thermally-formed oxide layer enhances hardness, wear resistance, and corrosion resistance in Ti and its alloy [2]. Surface modified by relatively simple thermal oxidation method demonstrated superior properties as it was easier, lower in cost, and generated thick and highly crystalline rutile oxide film [12]. It is widely known that surface roughness is a key parameter that affects wear and corrosion resistance of components [45].

Prior studies have applied the thermal oxidation technique to enhance structural characteristics, morphology, and tribo-characteristics of oxide layers on the surface material. K., Aniołek et al., [46] and Aniołek et al., [44] investigated the properties of oxide layer and modified the surface of Grade 2 Ti to discover that the size of the formed oxide particle was noticeably larger after oxidation at 600 °C, while Aniołek et al., [44] reported that at 600 °C, the oxide layer covered the entire examined surface, but in certain areas unevenly, while finer and more oxide particles formed after oxidation at 700 °C. According to Jamesh et al., [47] and Kumar and Narayanan [2], Cp-Ti sample oxidised thermally in air at 650 °C for 48 h formed oxide grains along with a thick oxide film. Samples oxidised for 24 h displayed formation of oxide grains with thinner oxide layer. The phase contents of the oxide layer at Ti-15Mo exhibited strong dependence on the treatment conditions, signifying a predominance of the rutile phase over the anatase phase at temperatures > 650° C and longer period of time >16h [48]. Wen et al., [49] assessed Ti using two-step treatment - surface mechanical attrition treatment (SMAT) combined with thermal oxidation process, which showed that it was the nature of the surface energy to be at the highest and for the rutile crystal layer to be formed on its surface. Next, Sun et al., [50] applied a combination of laser surface texturing and thermal oxidation to generate oxide layer on the surfaces of Ti with more optimum structure and performance. The outcomes showed that optimisation at TC4 surface treated with laser texturing and thermal oxidation gave excellent tribo-characteristics at 650 °C for 25 h. They also investigated the thermal oxidation method to solve issues related to release of ions by improving corrosion resistance and wear resistance in Ti alloys. Luo et al., [51] found that the film of rutile TiO₂ existed on the surface of Ti alloy after thermal oxidation at 700 °C in a mixture of nitrogen gas with 40% oxygen by volume ratio, whereas the bio-tribological test revealed that thermally oxidised Ti alloy exhibited low friction coefficient and high wear resistance, which indicated that the thermally oxidised Ti alloy could be a potential candidate for artificial joints. Jamesh et al., [52] analysed the corrosion behaviour of thermally oxidised Cp-Ti that was cooled under varied conditions (furnace, air, and water). The sample Cp-Ti at 650 °C exhibited faster cooling with formation of oxide scales on the surface without spallation, while those at 850 °C displayed faster cooling conditions with formation of oxide scales with spallation. The rapid cooling rate has no deleterious effect on the corrosion resistance of TO CP-Ti at 650 °C for 14 h, while the rapid cooling rate exerted deleterious effect on the corrosion resistance of TO CP-Ti at 850 °C for 6 h. Arslan et al., [53] studied the effect of surface roughness on mechanical, tribological, and corrosion properties of thermally oxidised CP-Ti. After thermal oxidation, the surface roughness values increased and the single rutile phase existed on the surface after oxidation, in which from observation, the oxygen diffused under the oxide layer. Furthermore, surface roughness had no effect on the preferred growth orientation of the rutile phase. While unstable and high friction coefficients were obtained with increasing roughness for untreated CP-Ti, this did not occur for the oxidised specimens. The result was similar after observing the corrosion behaviour. With decreasing surface roughness values, the corrosion potentials shifted to higher values.
3. Conclusion and Future Recommendations

Surface modifications are often performed on biomedical implants to improve corrosion resistance, wear resistance, surface texture, and biocompatibility [53]. Generally, the overall trends of surface modification methods seem to shift from the use of conventional source (chemical, induction heater, and gas) to the application of advanced technology (electrolyte-based, laser, plasma, and ion). This could be due to the low efficiency of conventional methods that require longer time and much energy. Studies on surface modification also appear to expand from focusing on tribological issues, such as wear resistance, corrosion resistance, hardness of modified layer, and enhancing the osseointegration of native materials used for spinal interbody spacers, to clinical issues, such as cell growth, cell attachment, and antibacterial effects. Such progression demands cutting-edge technologies in the future to offer solutions of dual issues simultaneously, i.e. tribological and clinical. Therefore, some techniques have been developed to achieve the required composition, thickness, and homogeneity of surface oxide layers as they play a great role in altering the corrosion behavior and biocompatibility of biomedical Ti materials. In addition, the human life may be can be reduce endangered due to ill-effect from corrosion in issues biomedical. It is inferred from the literature, that up to this day, an ideal combination of wear and corrosion properties is still a challenge as far as the application of Ti based materials is concerned in the biomedical field. Hence, further investigation can be extended to studying a new Ti-based alloy via thermal oxidation for surface modification.

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