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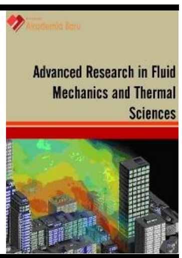

Hydroxyapatite and Thermal Oxidation as Intermediate Layer on Metallic Biomaterial for Medical Implant: A Review

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ABSTRACT

Preventing corrosion in bio implant is essential in overcoming allergic symptoms and inflammation as a result of biomaterial implants in human body. Upon contact with fluids, such as bloodstream, metal implants turn highly antagonistic, which leads to corrosion. Scientific findings have indicated that implant metals must go through surface modification to create a layer between metal surface and fluidic environment. This method has displayed good anti-corrosion performance. Surface modification is composed of three methods, namely mechanical, chemical, and physical modifications. This paper focuses on the chemical technique, which is the sol-gel dip technique, and thermal oxidation as the intermediate layer between hydroxyapatite (HA) and metal surface. A summary of recent progress related to sol-gel and HA research applications is presented as well. Combination of the two methods has shown good results in degradation ion activity.

1. Introduction

The use of biomaterials is common in medical implants (heart valves, stents, and grafts), biosensors, drug delivery, statures, bio electrodes, dentistry (tissue substitution & repair, and implants), and skin replacement [1-6]. After the first summit held on biomaterials at Clemson University in the USA in 1969, biomaterials were introduced to the scientific society and received significant attention due to the potential for increasing health among mankind [7]. The purpose of biomaterial implantation is to enhance body function, to replace damaged tissues, and to recover the structure of the organs [1].

Biomaterial refers to a nonviable material applied in the medical line for the purpose of interacting with bodily biological functions and systems [14]. Table 1 show the purpose of bio implant in medical field. According to Shen and others, biomaterials should possess the following properties

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to achieve the desired lifespan: biocompatibility, high wear resistance, high corrosion resistance, and good mechanical properties [9]. Tables 2 shows characteristic in order to be biomaterial implant.

Table 1
Summary Function of Bio Implant

Author	Function of bio implant	Examples
[8]	Aid tissue healing process	bone fractures
[9-11]	Replace damaged, diseased, or worn body parts	arthritic joints
[12]	Correct deformities	spine curvature
[9]	Simulate congenitally absent or unformed body parts	malformed ears
[13]	Improve the function of organs	heart valves

Table 2
Characteristics of Biomaterial

Author	Properties of Biomaterials	Explanation
[15]	Biocompatibility	Non-toxic and does not cause allergic reaction when implanted into the body. Ideal implants or their wear particles do not cause complication.
[11]	High Wear Resistance	Upon usage in artificial joints, only a few wear particles are produced, thus solving the primary issue of bio implants and prolonging the lifespan of artificial joints. It reduces volume loss to minimise the risk of wearing via polyethylene cup that increases the stability of prostheses.
[16]	High corrosion resistance	High corrosion resistance mitigates damage caused by corrosive wear, hence reducing wear rate. Metal alloys are popular for fabricating femoral heads, and the quantity of metallic ions released into synovial fluids is related to bio implant corrosion resistance. Prostheses, made of material with higher corrosion resistance, generate very few metal ions, thus reducing the possibility of allergic reaction.
[17]	Good mechanical properties	Hip or knee prostheses must bear 3—5 times the load of our body weight in vivo. The mechanical properties of biomaterials can withstand in vivo condition. Elastic modulus is crucial, but large modulus may cause bone atrophy, while high fatigue strength decreases the risk of catastrophic failure due to cyclic loading. Considering other mechanical properties (stiffness, hardness, and tensile & shear strength) is vital when selecting implant biomaterials.

Both design and selection of implants heavily depend on the application [3]. Due to optimum properties (mechanical strength, corrosion resistance, and biocompatibility), metallic implants are superior to polymer and polymer-ceramic composites [2, 18]. As for the orthopaedic field, use of metal implants is based on their usage as permanent implants (total joints replacement) and temporary implants (bone plates, screws, and pins) [2, 3]. It is vital to note that only some alloys and metals are suitable for bio implants [3]. Titanium, cobalt-chromium alloys, and stainless steel are some metals that suit permanent implants [2, 18]. As for metallic alloys in permanent implants, several issues have emerged, such as incompatibility between natural bones and metallic alloys in terms of mechanical properties, mainly due to higher elastic modulus in alloys [19]. Under in vivo setting, stress shielding may be caused due to implant and bone mechanical mismatch. Stress shielding refers to the more bulk load carried by the implant, while reduced load by the surrounding bone tissues [2]. Implants in human body may undergo a complex multifactorial corrosion process that relies on some parameters, namely metallurgical, solution chemistry, mechanical, and geometric [18]. This paper reviews titanium-based alloy and its anti-corrosion performance with thermal oxidation and hydroxyapatite (HA) sol-gel process.

2. Corrosion on Biomaterial Implant

2.1 Selection of Titanium-Based Alloy as Biomaterial

The selection of the metal as bio implant is one of critical factors that must be considered to ensure safe and retainable impacts for long term without negative effect. Titanium alloys are very popular biomaterials in the implant industry due to their properties of low density, relatively high strength, excellent biocompatibility, and corrosion resistance[20]. Titanium alloys are commonly applied for reconstruction of bones, inclusive of lumbar fixation & fusion, total knee arthroplasty (TKA), total hip replacement (THR), and dynamic compression plate (DCP) [21]. Titanium alloy is an exceptional candidate due to its excellent corrosion resistance, bio inertness, and high strength-to-weight ratio [22-25], in comparison to other metals, for instance, CoCrMo alloy and SUS316L stainless steel [22]. Ariffin added that titanium alloy has lower Young's modulus (110GPa), when compared to several other biomaterials, such as stainless steel and Co-Cr alloys [21, 22].

2.2 Type of Corrosion in Metal Implant

The process of corrosion refers to unstable changes in metal thermodynamically due to electrochemical oxidation of metal in reaction with oxygen. Corrosion occurs due to interaction with electrochemical cells that leads to varied reactions of corrosion [26-28]. Figure 1 shows type of corrosion and description in Table 3. Implants face severe corrosion environment due to electrochemical reaction between metal and human body fluid, which encompasses several constituents, such as sodium, water, proteins, chlorine, plasma, and mucin (saliva) [28].

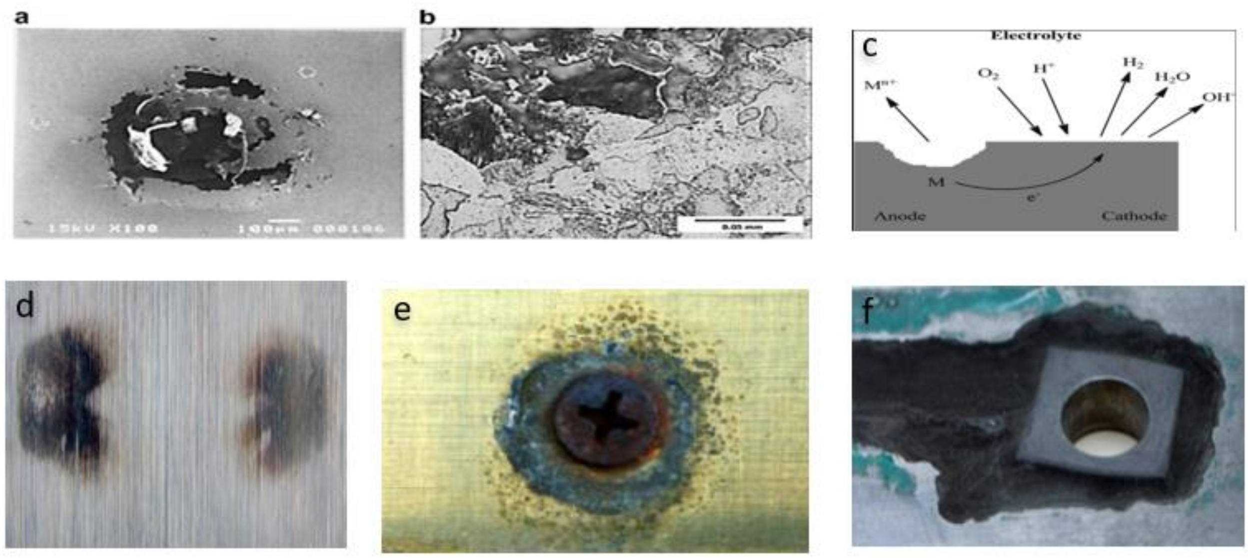

Fig. 1. (a) Pitting Corrosion (b) uniform Corrosion (c) Electrochemical Corrosion (d) Fretting Corrosion (e) Galvanic Corrosion (f) Crevice Corrosion

Table 3
Types of Corrosion

Author	Type of Corrosion	Detail/Description
[29]	Crevice Corrosion	Occurs in narrow region, such as implant screw bone interface. Metallic ions that dissolve create positive charge in the crevice
[23, 28]	Galvanic Corrosion	Occurs due to difference in the electrical aspect
[29]	Electrochemical corrosion	Both cathodic reduction and anodic oxidation deteriorate metal
[30]	Uniform Corrosion	Inevitable corrosion as all metal ions immersed in electrolytic solutions are condemned
[31]	Pitting Corrosion	Causes severe damages and releases vast metal ions. Pitting causes small holes/cavities at the material surface that may be hindered by applying an adherent, tenacious, and self-healing thin passive film.
[32]	Fretting Corrosion	When two opposing surfaces (bone plates and screw heads of prosthetic device) rub each other continuously in an oscillating way, small movements are generated between the contacting surfaces in corrosive medium.

2.3 Chemical Reaction and its Effect on The Human Body

Most metallic implants portray high corrosion resistance that can prolong their lifespan in human body. Corrosion does not happen rapidly as electrochemical reaction only takes place upon implanting the implants into the body. Release of metal ions in human body from implants has turned into a concern amidst patients and the biomedical domain [33-35]. These implants tend to discharge undesired metal ions that appear to be non-biocompatible. Corrosion deteriorates the lifespan of implants, which demands a follow-up surgery [35]. Release of metal ions may lead to several issues (metal allergy, granuloma, and carcinoma) [36], while severe complications and implant system failure due to massive metal ion release.

3. Surface Modification for Titanium Alloy

Although titanium alloys are widely used in implant manufacture, failure of fixation may still occur due to insufficient early osseointegration, infection, surgical trauma, premature overloading, improper surgical placement, fatigue, and poor quality bone surrounding the implants [23]. Successful implantation highly depends on biochemical, physical, mechanical, and surface topography characteristics of the implant surface [37]. Hence, surface engineering plays a significant role in enhancing implantation process [38]. Surface treatment or modification involves the creation of a barrier that serves as a wall that protects the metal from its environment[39]. This technique can overcome and improve the challenges noted in bio implant [40, 41]. Apart from recommending this method, many studies have focused on improving corrosion resistance, biocompatibility, and mechanical properties [1, 42]. Several surface treatments have been proposed, inclusive of mechanical, chemical, and physical methods.

3.1 Chemical Method

Chemical treatment of titanium and its alloys is mainly based on chemical reactions that occur at the interface between titanium and solution [43]. Some widely used chemical methods are acid treatment, hydrogen peroxide treatment, electrochemical treatment (anodic oxidation)[44], sol gel, and chemical vapour deposition (CVD) [43, 45]. Chemical method enhances biocompatibility, bioactivity, and osseointegration [46].

3.1.1 Sol gel coating

The combination of sol–gel preparation and dip-coating methods has been widely used for coating purpose on metallic biomaterials [47]. The sol-gel process refers to a technique that produces suitable solid materials that derive from small molecules to prepare varied coatings on surfaces of titanium-based materials. This incorporates small molecules (precursors) converting into colloidal solution (sol), and later, integrated network (gel) that contain network polymers or discrete particles [48]. This sol-gel technique has several benefits, namely enables coating on complex shapes, low processing temperature (prevents volatilisation of entrapped species), and compounds usage without any impurity in the end-product [47, 48]. On the other hand, some drawbacks of this method are extended processing duration, and challenges in phase separation during synthesis of hybrid coating [48]. In fact, it is only recently that the sol-gel method has been applied in the biomedical domain. This method can be used to coat thin ceramics (< 10 µm), allows better control of microstructure and chemical composition in coating, homogeneous films preparation, lower temperature for densification, cost-effective, and simpler tool [43]. The chemicals applied for coatings on titanium alloys for biomedical area are calcium phosphate (CaP), titanium oxide (TiO_2), and TiO_2–CaP composite. Several coatings based on silica have been generated via sol-gel method. Here, the sample is dipped in solution that has precursors, and later, withdrawn at a constant speed using motor. Deposition of solid film is obtained from gravitational draining, solvent evaporation, and condensation reactions.

3.1.1.1 Hydroxyapatite

Hydroxyapatite (HA) [Ca10(PO4)6OH2] has been extensively used in the biomedical area, such as dentistry and orthopaedics, mainly due to its similarity to bone mineral composition, as well as exceptional biocompatibility and osteoconductive [49]. The HA has biocompatibility with soft tissues (skin and muscle) and hard tissues (gum). The HA coating on Ti alloys substrate has garnered much attention due to their excellent mechanical properties and biocompatibility [50]. Meanwhile, some shortcomings of HA in load bearing (as hip bone, and knee joint) implant are low fracture toughness (≤ 1 MPam), brittleness, and poor HA mechanical properties when compared to cortical bone [51, 52]. It is common to generate load bearing implants using metals (e.g., Ti and its alloys), mainly because they have exceptional mechanical properties [53]. Due to this reason, HA has become a preferred choice to be applied on metallic substrate, such as Cobalt-based alloy, stainless steel, and titanium, as implants. This reflects on the combination of metal components that exert superior mechanical properties with exceptional biological response deriving from HA bio ceramic [40]. Coating HA on metallic alloy has demonstrated essential enhancement in bioactivity aspect. Recent research has shown attractive improvements, such as coated titanium samples with biomechanical and bio-functional equilibrium, inclusive of its potential use in biomedical applications (partial replacement of bone tissue) [54], as well as HAp and OCP coatings that suppress corrosion and foreign-body reaction in vivo [55]. Besides, HA coating deposited using this approach promotes low solubility and stability, thus minimising healing period [46]. Nonetheless, direct HA coating on metal substrate could lead to crack surface, delamination, and dissolved HA coating layer at in vivo and in vitro investigations [46]. Table 4 below shows the summary if previous study on hydroxyapatite.

Table 4
Summary of Previous Study on Hydroxyapatite on Bio Material

Author	Objective/Aim	Experiment setup	Findings
[56]	Study the effect of two coatings on biocompatibility and corrosion behaviour of Ti-6Al-4V biomedical implant material	Pre-Treatment Ti-6Al-4V disk-shaped specimens each measuring 12mmx9mmx5mm were prepared. The specimens were polished by different grades of silicon carbide papers (180-1200 grit) followed by cloth wheel polishing with alumina paste on a polishing machine. These specimens were washed with de-ionized water followed by acetone rinsing. Surface Treatment The substrates were grit blasted with alumina (Al2O3) in accordance with normal thermal spray. The air-blasted specimens were then coated with the HA and HA/TiO_2 powders using HVFS technique	The results showed that both the HA, as well as, the HA/TiO_2 coatings significantly increased the corrosion resistance of the substrate material. The HA coating was found to be more biocompatible as compared to the un-coated and HA/TiO_2-coated Ti-6Al-4V alloy
[57]	To improve biocompatibility and corrosion resistance during the initial implantation stage, zinc substituted hydroxyapatite (ZnHAp) coating was fabricated on pure titanium	Pre-Treatment A pure titanium plate with 99.9 % purity with dimensions of 10 x 10 x 1 mm^3.All samples were ground 280, 500, 800 and 1000. The samples were cleaned using anhydrous ethanol and deionized water in an ultrasonic cleaner about 25 s and then ultrasonically washed in anhydrous ethanol and deionised water in an ultrasonic cleaner. Finally, the polished and etched Ti plates were soaked in 50 mL of a 5 M NaOH aqueous solution, kept at 60^0C for 24 h and then dried in a warm stream of air at 80^0C for 1 h. Surface Treatment A Ti plate pre-treated with NaOH solution was used as the working electrode. The ZnHAp coating was conducted in an electrolyte composed of 4.2 x 10^{-2} M Ca $(NO_3)_2$, 2.5 x 10^{-2} M, NH_4,H_2PO_4 and 5 x 10^{-2} M $Zn(NO_3)_2$. The parameter values were pH 4.4 ± 0.5, 0.9 $mAcm^{-2}$ current density, 20 min and 65^0C.	The prepared coatings were completely crack-free and were uniform with few Zn incorporations. The addition of Zn^2 into the HAp significantly reduced the porosity, thus, the ZnHAp coating became much denser. The results revealed that the ZnHAp-coated Ti samples with a smooth topography and a lower corrosion current density led to a lower Ti corrosion rate, which was accompanied by an excellent bioactivity.
[58]	To study, HAP coatings were deposited from pure HAP targets on Ti6Al4V substrates using the radio frequency magnetron sputtering technique at substrate temperatures ranging from 400 to 800◦C.	Pre-Treatment Ti6Al4V alloy discs (10 mm diameter) were used as substrates. The Ti6Al4V alloy discs were mechanically ground using grit 4000, then polished with diamond paste until reaching a mirror-like surface finishing with an average roughness of 40 nm	All the coatings supported the attachment and growth of the osteosarcoma cells the best cell viability was observed for the HAP films grown in the 700–800◦C range. Comparing the investigated coatings, those prepared at 700 and 800◦C revealed the highest

		Surface Treatment The coatings were prepared using a RF magnetron sputtering unit equipped with one cathode made of HAP. The deposition parameters were: the base pressure = 1.3 × 10−4Pa, Ar working pressure = 6.6 × 10−1Pa, target power fed = 50 W, substrate bias voltage = −60 V, substrate temperature = 400, 500, 600, 700, 800◦C, deposition time = 360 min. The thickness of the coatings was of about 450 nm.	corrosion resistance in saliva and the best biological properties
[59]	Effect of the calcium acetate concentration in the electrolyte used to anodize CP Ti on the composition, structure, and corrosion behaviour of the anodic layers.	Pre-Treatment Commercial pure titanium samples were cut into square forms of 10x10x1 mm. Sample were cleaned in an ultrasonic bath with acetone for 3 min, etched in Kroll's reagent (1 ml HF and 5 ml HNO3 in 44 ml H2O) during 10 min, and cleaned again in an ultrasonic bath for 10 min in propanol followed by 5 min rinsing in distilled water, and then dried with warm air. Surface Treatment The electrolyte used for the anodic treatment consisted in a solution of β-glycerophosphate disodium salt pentahydrate (β-GP) at different concentrations of calcium acetate monohydrate (CA). DC power supply was used and the treatment was carried out at room temperature for 1 min at 300V during anodic treatment. A platinum plate was used as cathode (2cm^2). The distance between the cathode and the anode (Ti plates) was kept constant (8 cm) for each treatment. The surface area of the titanium samples exposed to the electrolyte solution was 0.358 cm2. All the anodic treatments were done under agitation in a turbulent regime by using a magnetic stirrer rotating at 200 rpm	The corrosion resistance was improved by the surface treatment, with both concentrations of calcium acetate, when compared with untreated titanium.

3.2 Thermal Oxidation as Intermediate Layer

Beyond doubt, sufficient mechanical interlocking, as well as chemical reaction between substrate and coating, can enhance bonding adhesion [60]. Using strong alkaline chemicals can generate intermediate layer, but managing chemical waste to preserve the environment can be rather costly. Hence, a pressing need is present to propose an environment-friendly and cost-effective surface treatment to enhance the quality of HA coating on metal. Thermal oxidation is a technique that generates intermediate layer that bridges metallic implant and HA coating [60-62]. Mas Ayu and team looked into the effects of oxide interlayer on cobalt-chromium-molybdenum. In enhancing the HA coating quality and the cell responses, the substrates were oxidised between 850 °C and 1050 °C for 3 hours. The outcomes displayed that the rough oxide interlayer surface offered better mechanical interlocking of HA particles with surface of substrate, minus visible micro-cracks. Additionally, HA-coated substrates with oxide interlayer seemed to project better cells proliferation and strong attachment, in comparison to those without oxide interlayer[60]. Similarly, Ciobanu and Harja assessed an alternative coating approach via biomimetic technique in producing HA layers on the surface of titanium, along with thermal oxidation pre-treatment to enhance the aspect of bioactivity on titanium surface. Next, the titanium implants were coated with HA layer under biomimetic settings using Simulated Body Fluid (SBF) solution. The alkali-treated titanium oxide coating had induced HA formation on the surface of titanium after incubation in SBF solution. The findings showed that the treatments had successfully induced formation of HA on titanium surface [60]. Despite developing varied interlayer types for differing material substrates, investigation into titanium alloy is intriguing, especially studies pertaining to this substrate in combination with oxide interlayer prior to HA coating are in scarcity. Previous studies reported that addition of oxide interlayer on titanium alloy via thermal oxidation technique minimised cracks in HA, as well as its exceptional impact upon anti-corrosion performances. Table 5 below show the summary research on thermal oxidation by researcher.

Table 5
Summary of Previous Study on Thermal Oxidation on Bio Material

Author	Objective/Aim	Experiment setup	Findings
[45, 56]	Study the effect of thermal oxidation in term of hydrophilicity and corrosion resistance	<u>Pre-treatment</u> Commercial titanium foils with 99.99% purity and 0.10-mm thickness cut into 1 × 1 cm2, ultrasonically cleaned in acetone, ethyl alcohol, and deionized (DI) water for 10 minutes each, rinsed with DI water and dried using N2 gas. <u>Surface Treatment</u> The thermal oxidation process of titanium foils was conducted in air at varied temperatures ranging from 300°C, 400°C, 500°C, and 600°C with the heating rate of 10°C/minute and held at the designed temperatures for 3 hours. Then, the samples were left to cool down to the room temperature.	The most improvement in surface roughness was found in the specimens treated at 400°C, which significantly improved surface hydrophilicity. But both surface roughness and hydrophilicity reduced when oxidized at 500°C and 600°C, suggesting that hydrophilicity was dominated by the surface roughness. In addition, this surface treatment did not reduce the biocompatibility of the metallic Ti substrates against murine osteoblasts
[57]	Study the effect of carbon content (0.03% and 0.24%) of oxidized Co-Cr-Mo	<u>Pre treatment</u> Two different carbon contents 0.03%C and 0.24%C of Cobalt-Chromium-Molybdenum alloy (Co-Cr-Mo) cut using a precision cutter into disc size of 14mm diameter and 2mm. All samples were ground obtain similar surface roughness. The surface roughness of all substrate was measured surface profilometer while the average roughness of ground samples obtained was 0.1±0.02 µm. Ground samples were left to dry for	A high carbon content sample generates a lower corrosion-rate compared to low carbon content sample even though all samples were treated at similar oxidation temperature and time duration.

		overnight in the oven at 50ºC before they were taken for next process. <u>Surface Treatment</u> All samples were placed on the crucible holder and then heated at constant temperature of 1050ºC for 6 hours duration in a muffle furnace under atmospheric condition	
[58]	Study an oxide interlayer on Co-Cr-Mo alloys was developed through thermal oxidation prior to HA coating with the objective to provide better anchorage of HA coatings on the substrate surface, reduce metal ions release and at the same time enhancing the cell attachment.	<u>Pre treatment</u> Cut Co-Cr-Mo Alloy into small discs size of 14mm x 2mm. Sample then annealed at 1121°C for 1 h under atmospheric condition and cooled inside muffle for 4h. All samples were ground to obtain similar surface roughness. The surface roughness of all substrate was measured while the average roughness of ground samples obtained was 0.1±0.02 µm <u>Surface Treatment</u> The thermal oxidation process was conducted in a muffle furnace at different temperatures (850°C, 1050°C and 1250°C) for 3 hours to create an oxide interlayer on the substrate surface	HA coated substrates with oxide interlayer demonstrate strong attachment and proliferation of cells than the HA coated substrates without oxide interlayer. It is concluded that the introduction of an intermediate oxide layer on Co-Cr-Mo substrate prior to HA coating has shown a positive effect in terms of increment of the adhesion strength of HA coating
[59]	To increase the bioactivity of Titanium implant	<u>Pre-Treatment</u> Titanium bar was cut as rectangular strips with typical dimensions of 10 mm x 10 mm x 3 mm. The samples were mechanically gritted with silicon carbide paper and polished using 60- and 180grit SiC paper followed by chemical etching in 1 % HF solution for 2 min <u>Surface Treatment</u> The samples were treated by an anodization process using an electrochemical cell. Anodization of Ti sample was performed under constant cell voltage. The Ti substrates were introduced in the cell and the initial current density was 5 mA/cm2. Afterwards, the samples were cleaned with deionised water. The samples were then immersed into 0.5 M NaOH solution at 160 °C in a pressure chamber for 24h with a heating rate of 5 °C/min. The samples were subsequently washed in deionized water for 5 min and finally heat-treated at 600 °C for 3 h in a furnace with a heating rate of 5 °C/min.	All the alkali-treated titanium oxide coatings could induce hydroxyapatite formation on titanium surface after incubation in SBF solution. The obtained results indicate that these treatments can induce the hydroxyapatite formation on the titanium surface

4. Conclusion

This review article focuses on the surface modification and technique to improve anti-corrosion performance of Titanium Alloy as a bioimplant material. It is compulsory for all implant materials to undergo surface treatment as this material, as proven by many researches and investigations, can corrode without adequate surface improvement. This is because; chemical reaction with blood promotes corrosion in metal implants. Many surface treatments have been performed since the past century, although it is not perfect and has long-term effect. The dip technique of sol-gel, along with HA as the medium for coating, has been reviewed by placing focus on the microstructure and its performance in bioimplant. This technique is non-intricate and involves low processing temperature. It is also considered as the most flexible and promising technique in preparing high-quality HA films on metal substrate with long-term stability. Nevertheless, the direct coating of HA on metal substrate seems to cause delamination, crack surface, and dissolution of HA coating layer. In order to address these issues, thermal oxidation may be integrated as the intermediate layer while preparing the sample. In fact, prior studies have reported enhancement in corrosion and wear resistance upon treatment of thermal oxidation. Nevertheless, no study has looked into the effectiveness of HA coating with oxide interlayer on titanium alloy, as well as its performance in anti-corrosion test.

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