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Surface Modifications of Titanium Materials for developing Corrosion Behavior in Human Body Environment: A Review

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Abstract

Apart from ceramics, polymers, and composites, metallic materials rank distinguished in the field of biomaterials. Recently, titanium (Ti) based materials are attracting much interest as implantable materials because of their superior corrosion resistance, better mechanical properties such as remarkably high specific strength, low elastic modulus, and excellent biocompatibility compared to other competing biomaterials like stainless steel, Co-Cr alloys and nitinol alloys. Implantable Ti based materials must have high corrosion resistance to withstand the degradation which results from the reactions with the hostile body environment and does not result in adverse biological troubles in the body. At the same time, Ti materials must be stable and retain their properties for a long time reliably. The present article discusses the importance of creation of stable, compact and continuous oxide layers on the surface of Ti materials has been strongly effective to combat corrosion in aggressive body fluid. In this review, the traditional and advanced surface modification techniques that be used to increase the bioactivity of the Ti surfaces and in turn to improve the corrosion behaviour have also been discussed at length.

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Keywords: Corrosion; biomedical applications, titanium alloys, surface modification techniques.

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1. Introduction

The application of biomaterials in the ancient times has been practiced more as an art and entirely lacked in terms of scientific knowledge until advanced attempts from researchers and scientist were made recently to develop this field of engineering medical sciences. Of late, 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. The research on biomaterials initially started by testing of these materials on animals and their acceptability on the human body system were indirectly established. 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 et al. 1984). Nowadays, the mainly familiar kinds of materials used in biomedical applications are Metals, Ceramics, Polymers, and Composites. It is well known that prosthetic devices and components need to fulfill several imperative requirements so that they are successful in service over a long-term usage in the body without rejection and minimal failure. Titanium has been commercially offered during last more than 60 years and since then several titanium based materials have been developed as a surgical material until 1960. However, mid 1970s, has witnessed path-breaking developments in the advancements on Ti based biomaterials have been increasing gradually (Williams, 1984; Luckey and Kubli, 1983; Gonzalez and Mirza-Rosca, 1999). Titanium and its alloys , so far, have proved to be the most befitting materials for biomedical applications due to their particular characteristics such as better mechanical properties, excellent biocompatibility and superior corrosion behavior [Linder et al, 1988]. There exists, yet, an inevitable fact that nearly all metallic materials electrochemically corrode to some degree when they come in contact with hostile/aggressive fluid under certain conditions. Therefore, corrosion in two forms, general and localized, is one of the main problems of metallic biomaterials. Consequently, it has become the most important parameter when it comes to choosing the materials for surgical implants in hostile solutions which simulate the media of the human body. Degradation of material and released ions are the most common consequence of reaction between body fluids and implant which result in several problems including inflammation, formation of foreign body giant cells (Lo´pez et al., 2001), and may cause loosening of implant from the bone (Urban et al, 1994) due to osteolysis (Laing et al., 1967). The health facts of such nature have been widely reported in the literature (French et al., 1984; Alberktsson et al, 1983). The researchers reported that release of metal ions adversely effects the healing of bone and the surrounding tissues. In addition, corrosion of the implant itself is bound to affect the essential properties of the implant such as fatigue life and tensile strength leading to the poor mechanical compatibility and eventually may result in inevitable failure of the implants (Jacobs et al., 1998). Hence, controlling and protection of an implant material from corrosion are basic and indispensable demands. Ti based materials are regarded as highly corrosion resistant mainly due to the strong passive oxide film formation at room temperature on their surface. This film, which largely consists of TiO_2, protects material and provides chemical inertness in different media. Nevertheless, titanium's passive state is not entirely stable and under certain conditions, localized breakdown on a highly microscopic scale has been found to occur. Consequently, a strong destructive attack may occur on the surface of material due to its reaction with hostile environment. Any deficiency in the performance of the titanium's surface film is severely harmful to the corrosion behavior as well as on other required characteristics. Therefore, surface modification is often performed in order to enhance its mechanical, biological and chemical properties.

The importance of the subject, increasing research interest and huge unexplored potential is the driving force behind this literature review. The present review study has been done with a view to provide the researchers in the field to have a bird's eye view on the hotspots on research in the surface modification methods and techniques for improving corrosion behavior of Ti alloys in human body fluid. The corrosion mitigation of biomedical Ti materials by surface modification techniques is discussed in this paper with a focus to present the state of the art.

2. The importance of titanium oxide layers

It is well known that corrosion and surface layer dissolution are two mechanisms responsible for release of additional ions in the body from the implants. Extensive release of metal ions from human body implants can result in adverse biological reactions and even lead to mechanical failure of the device. It is generally acknowledged that the biocompatibility and susceptibility of metals to different kinds of corrosion and the rate at which these processes occur are closely related to the quality of the passive film on the metal surface (Szklarska-Smialowska**,** 1986). Titanium develops a very strong passivating oxide layer which forms naturally on the surface (Souto and Burstein, 1996). Typically, the passive layer on titanium has a thickness in the range of 2-5nm (Casillas et al, 1994; Sitting et al, 1997; Lausmaa, 1996; McCafferty and Wightman, 1999). Despite the adherence of the surface layer to its metal substrate and its ability to reform readily when damaged, Ti has occasionally been observed in tissue adjacent to implant prosthesis (Ducheyne et al, 1984). The actual composition of Ti oxide layer consists mainly of TiO_2 (rutile) stiochiometry (Bessho et al., 1995; Pankush et al, 1993; Ohtsuka et al, 1986) accompanied by some Ti_2O_3 and TiO (Sitting et al. 1997; , Delplancke and Winand, 1988). Corrosion resistance of Ti alloys can be improved by addition some of elements like Zr, Nb and Ta through stabilization of the surface oxide films in biological environment (Okazaki et al., 1997) and formation of ZrO_2, Nb_2O_5 (Yu and Scully, 1997) and Ta_2O_5 (Okazaki, 2001) strong oxides respectively. Ti with these alloying elements exhibits better corrosion behavior than the stainless steel AISI 316L and a wrought CoNiCr alloy (Zitter and Plenk, 1987). On the other hand, the repassivation rate of titanium is fast as it belongs to the high reactive metal group, which quickly forms an oxide layer in air or in normal tissue fluids (Collings, 1984). Further, the repassivation rate of titanium was found to be slow in biological systems as compared to saline (Hanawa et al., 1998). Eventually, the significant difference of biocorrosion behavior of titanium materials is cause by different properties of the surface layer.

3. Corrosion mitigation in biomedical titanium materials by surface modification techniques

In fact, surface characteristics play a vital role to improve the service life of metal implants. In principle, engineers and scientists have been seeking diverse techniques to develop the biocompatibility and the corrosion behavior of metal implants, aiming to make them adapt to the implant environment better (Han et al., 2003; Sun et al., 2005; Nie et al., 2000; Gu and Chen, 2006). Therefore, surface modification becomes one of the most attractive branches in the field of biomaterial research. Several methods can be used to improve the performance of implants in biological fluid such as inhibitors, cathodic protection, anodic protection and many others. But in an extremely sensitive and complex bio system, the performance of implants after treating it by all these methods may not be feasible. Surface modification techniques are the most viable alternatives for increasing corrosion resistance and related properties of biomaterial surfaces. Superior corrosion behavior, improved wear resistance, better osseointegration rate, high biocompatibility and enhanced aesthetics are most important characteristics which can be attained through surface modification. Some examples of surface modification processes which can be employed to improve the corrosion behavior and other desirable properties of bio-grade Ti are: physical and chemical vapor deposition, laser cladding, thermal oxidation and thermal spraying, plasma spray, ion implantation, micro-arc oxidation, sandblasting and electrochemical treatment (Zhou et al, 2007; Liu et al., 2004; Vadira and Kamaraj, 2007; Zherebtsov et al, 2009; He et al., 2007; Cassar et al., 2010; Wang et al., 2009; Liu et al., 2008; Jiang et al., 2006; Guilherme et al., 2005; Arenas et al., 2000). The subsequent text presents literatures which have make important attempts in improving the corrosion behavior of biomedical Ti materials using surface modification techniques.

Commercially pure titanium (CpTi) is widely used for hard tissue replacement owing to the fact that it possesses properties which match best to the requirements of biomedical applications, except wear resistance when used for artificial hip joints. In order to improve wear resistance and corrosion behavior, various nitriding techniques including diffusion, ion-plasma, detonation, laser and high-energy methods have been employed to synthesize TiN surface layers. The nitrogen ion implantation technique is an excellent method to develop passivity and to increase the corrosion resistance as well. This is due to the fact that the formation of TiN and Ti_2N phases suppress the migration of ions and stabilize the growth of TiO_2 layer on the surface of Ti based materials (Mudali et al., 2003; Sundararajan and Praunseis, 2004). Nitrogen ion implantation makes the Ti surface wear-resistant by forming nitrides (TiN; Ti_2N) apart from TiO_2. This technique has been performed at specific energies to achieve nitride phase with surface hardness, wear resistance and corrosion behavior in various doses (Arenas et al., 2000; Fukumoto et al., 1999). Fulazzaky et al. (Mohamad et al., 2012) have made among one of the most recent attempts to implant nitrogen ion on the CpTi-VT1-0 in various doses and energies. They reported the formation of a crystalline nitride phase (TiN) with relatively uniform particle size distributions. They found that with increasing doses, the nitrogen ion implantation improved the corrosion resistance of the CpTi surface, except for the CpTi implanted at lower doses (80 keV). In addition, the Ecorr change was found to be less significant at higher energies and the optimal surface properties of the CpTi were implanted with nitrogen ions at doses between $\mathbf{1.0 \times 10^{17}}$ and $2.\mathbf{0} \times \mathbf{10^{17}}$ions/cm^2 using the implantation energy of 100 keV.

Plasma immersion ion implantation (PIII) is another surface modification process in which ions such as nitrogen, carbon and oxygen can be implanted on titanium based materials to improve their desirable properties by forming a hard layer on the surface. The implanted layer can further work as an interlayer for deposition of next layers with improved adhesion. Several studies have been performed using PIII with nitrogen and carbon which form nitrides and carbides (Xuanyong et al., 2004; Chenglong et al., 2007; Tang et al., 1998) and interlayers of different preferred composition such as Si, Ti, TiC, TiN, TiCN and Mo (Xuanyong et al., 2004; Walter et al., 1997). Mohan et al. (Mohan et al., 2012) studied the corrosion behavior of the β-21S titanium alloy (Ti–15Mo–3Nb–3Al–0.2Si) by implanting carbon ions using PIII. They used methane to supply carbon which produced diamond like carbon (DLC) deposit by radio frequency (RF) plasma enhanced chemical vapor deposition (PECVD). It well established that DLC is an ideal material for coating as it can provides chemical inertness, corrosion and wear resistance. They concluded that implantation of carbon over titanium alloy β-21S leads to the formation of Ti and Mo carbides and a thin DLC coating. The implanted layer also helps in depositing an adherent DLC coating on the otherwise difficult to coat titanium alloy. They reported that the electrochemical behavior of the implanted layer in simulated body fluid was poorer than the substrate; however, the corrosion resistance was nearly restored by the deposition of DLC coating on the implanted layer. Thus, the duplex treatment can be advantageously used to coat biomedical titanium alloys with biocompatible DLC coatings which are known to have low friction coefficient and high hardness.

Surface modification of metal implants using lasers can elicit specific, desired and timely response from the surrounding cells and tissues. This technique offers several advantages such as high speed, low processing time, easy to coat complex geometry and simple in tailoring the surface composition. Therefore, laser-etching techniques are also used to induce many useful surface properties such as uniform microstructures with significantly improved mechanical and tribological properties, biocompatibility and high corrosion resistance (Suzuki et al., 2000; Picraux and Pope, 1984). Moreover, laser processing is also used to create a good osseointegration rate as this gives high degree of purity with sufficient roughness on the surface of the implants (Hsu et al., 2007). The laser-treated Ti6Al4V alloy possesses better corrosion resistance than the base metal in different environments like Hank's solution. Typically, Yue et al. (Yue et al., 2002) used the excimer laser to modify surface of the Ti-6Al-4V alloy to improve corrosion behavior for dental applications. They found that processing increased the corrosion resistance in the alloys by seven folds. Recently Singh et al. (Raghuvir Singh et al., 2011) used Nd: YAG laser for surface modification on calcium phosphate coated Ti–6Al–4V. They used varying laser power densities (25–50 W/mm^2) in simulated body condition (Ringer's physiological solution) and reported an improvement in the corrosion and mechanical behavior. They reported an increase in the passive current density of Ti–6Al–4V after laser modification at power densities up to 35 W/mm^2, after which it exhibited a decrease. A reduction in the passive current density (by more than an order) was observed with an increase in the laser power density from 25 to 50 W/mm^2. There is a growing interest in the development of a new generation materials such as β type titanium alloys composed of biocompatible elements such as, Nb, Zr, Mo, Ta and Sn (Kuroda et al., 1995). Geetha et al. (Geetha et al., 2004) carried out surface modification on β-alloy Ti-13Nb-13Zr in nitrogen atmosphere by using Nd: YAG laser in simulated body condition. They found that the corrosion resistance of laser nitrided samples was significantly better than the untreated alloy. In another research, Sasikumar et al. (Sasikumar et al., 2011) performed chemical and thermal treatments on the surface of β-alloy Ti-15Mo to improve the biocompatibility and corrosion resistance. The surface morphological studies of alkali and heat-treated β -Ti alloy showed a uniform, well defined nanoporous layer and flake-like structure. The vitro characterization revealed the formation of apatite-like particles over the entire surface of alkali-treated β-Ti alloy. The electrochemical studies indicated that the alkali-treated β-Ti alloy after 10 days of immersion in simulated body fluid solution exhibited very low current density and excellent corrosion resistance as compared to alkali heat-treated and untreated β-Ti alloy.

In recent years, nanotechnology approach also finds increasing interest in the researchers to improve the corrosion behavior of biomaterials. The technology is largely used for uniform coating of organic or inorganic nanoparticles on the surface of substrate (Carbajal et al., 2001; Shen et al., 2005). Nanoparticles are the ultrafine particles having diameters in the range of 1–100 nm which provide higher surface-to-volume ratio with decreasing particles size (Wang et al., 2006). The nanoparticles also enhance chances of selective oxidation which forms defensive oxide layer with greater adhesion to the surface of biomaterial. Moreover, the nanostructured materials are well-known for their outstanding mechanical and physical properties as a result of their extremely fine grain size and a high grain boundary volume fraction (Saji et al., 2007). The researchers have used various surface treatment processes to produce a nanorough surface on implants, such as nanophase titania, alumina, and hydroxyapatite (Webster et al., 1999; Webster et al., 2000; Bigi et al., 2007; Sato et al., 2008), nanoporous membranes [Webster et al., 1999), fibers with nano-scale diameter (Webster et al., 2000; Bigi et al., 2007) etc. A number of studies and researches revealed that the implant surface technologies have been developed from micro to nanoscale [Webster et al., 1999; Webster et al., 2000; Bigi et al., 2007; Sato et al., 2008; Swan et al., 2005; Elias et al., 2002; Webster et al., 2005; Rice et al., 2003; Li, 2003; Mendon et al., 2008). Yu, et al. (Wei-qiang et al., 2009) found that pure titanium with TiO_2 nanotube layers was effective in enhancing passive layer resistance and reducing the corrosion current density in naturally aerated Hank's solution compared to the smooth-Ti. In addition, they also reported that titanium with TiO_2 nanotube layers provided adequate electrochemical behavior for use as a dental implant material. According to Semak and Dahootre (Semak and Dahotre, 1998) the nanocrystalline diamond coated Ti-6Al-4V offered significant protection against electrochemical corrosion in a biological environment. Zaveri et al. (Nikita Zaveri et al., 2010) evaluated the corrosion behavior of Ti–6Al–4V coated with nano-TiO_2 in three simulated biofluids. They performed Tafel analysis for I_{corr}, E_{corr} and corrosion rates for bare and the laser treated specimens and found that the TiO_2 nanoparticle-coated Ti–6Al–4V is more corrosion resistant than the bare. The electrochemical impedance spectroscopy (EIS) indicated that the film formed on the Ti–6Al–4V alloy was comprised of a bilayered oxide consisting of the outer porous layer and an inner barrier; the latter reported to be mainly responsible for the corrosion resistance. Richard et al. (Richard et al., 2010) proved that the corrosion resistance and fretting wear of Cp Ti increases several folds on coating it with mixtures of nanoceramics (Al_2O_3 - TiO_2).

More recently, the formation of titanium oxide nanotubes on the Ti materials surface is found to be important in improving the cell adhesion and proliferation in biomedical applications. Self organized porous TiO_2 approximately 100 nm in diameter and 500 nm long have been formed in various electrolytes containing fluoride (Zwilling et al., 1999; Tsuchiya et al., 2005; Jeong et al., 2009; Lee et al., 2009; Kim and Choe, 2009). There are a number of parameters such as applied voltage, current density, anodization time, alloying element and electrolytes which affect the nanotube size and morphology suitable for clinical use. Kim et al. (Won-Gi and Han-Cheol, 2012) investigated the electro-chemical characteristics of Ti–30Ta–xZr (x = 3, 7 and 15 wt%) coated with nano-sized bio-TiN. They studied the electrochemical characteristics using the magnetic sputter and electrochemical methods. The reported that the formation of oxide nanotubes was achieved by anodizing a Ti–30Ta–xZr alloy in H_3 PO_4 electrolyte containing small amounts of fluoride ions at room temperature. They demonstrated that the corrosion resistance of the TiN-coating on the anodized Ti–30Ta–xZr alloys was higher than that of the untreated Ti alloys.

The available literature reveals that the Ti surface modified by the relatively simple thermal oxidation technique demonstrates superior properties than the others since it is easy and low-cost, and can produce thick, highly crystalline rutile oxide film (Bloyce et al., 1998). It is well known that the surface roughness is a key parameter affecting wear and corrosion resistance of components. Arslan et el. (Arslan et al., 2010) investigated the tribological and corrosion behavior of commercially pure titanium (CP-Ti) with different surface roughness values after thermal oxidation treatment. They produced a thick oxide layer on the Cp-Ti surface by heating at 850^{o}C for 8h in an O_2 atmosphere and demonstrated an improved corrosion and tribological behavior. They also observed that the surface roughness had a significant effect on these characteristics. Further, they reported that a decreased roughness improved the tribological and corrosion properties.

Anodic oxidation of titanium is regarded as an effective surface coating technology and has also been widely used for surface modification of bio-implants. The creation of porous titanium oxide films by dielectric breakdown provides improved film adhesion to the substrate and helps in achieving high-quality films by varying the electrolytes, temperature, alloying element, voltage, current density and time (Zwilling et al., 1999; Jakubowicz, 2008). Also, anodizing process can increase the oxide thickness to develop corrosion resistance and in turn decrease the release of ion (Song et al., 2007). The effect of electrochemical anodizing on corrosion resistance of Ti–(10-40wt%)Hf alloys was investigated by Jeong et al. (Yong-Hoon et al., 2011).They reported that the anodized Ti–xHf alloys exhibited better corrosion resistance than non-anodized Ti–xHf alloys. They attributed the improvements in corrosion resistance to the presence of hafnium.

4. Conclusion

The field of biomedical materials plays a significant role in manufacturing of a variety of biological artificial replacements which are very common in the modern times. Among bioimplantable metals, Ti and its alloys offer the best corrosion resistance compared to other competing materials such as Cr–Co, Ni–Ti, and SS316L alloys. Moreover, Ti and its alloys are the materials of choice in biomedical devices and components since long time, as these materials posses superior properties and performance especially biocompatibility and corrosion behavior. Corrosion is the first and foremost consideration for a material of any kind that is to be used in the body due to the corrosive nature of the body fluid. Its effect is unavoidable causing release of metal ions which affect the health adversely. Corrosion can reduce the life span of implanted device and consequently may impose revision surgery. In addition, the human life may be endangered due to ill-effect of corrosion. Even though Ti materials are characterized with spontaneously formation of protective uniform and adherent oxide film, their corrosion in simulated body fluid with releasing ions can cause serious health problems in bio-applications. Surface modification treatments have been used to modify the surfaces to enhance the corrosion resistance and biocompatibility of Ti materials. Several tradition techniques have been adopted to improve electrochemical characteristics and in turn the life span of implants such as nitride ion implantation, Plasma immersion ion implantation, thermal and anodic oxidation etc. Moreover, cutting edge techniques like laser and nanotechnology 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. It is inferred from the literature, that up to this day, an ideal combination of corrosion properties is still a challenge as far as the application of Ti based materials is concerned in the biomedical field. Therefore, classified literature presented in this paper is expected to confer a road map for an interdisciplinary approach in the design and control of surface modification techniques that used for improving corrosion behavior of biomedical Ti materials.

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