



Review

Corrosion and surface modification on biocompatible metals: A review

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ARTICLE INFO

Article history:

Received 7 December 2016

Accepted 18 April 2017

Available online 20 April 2017

Keywords:

Biocompatible metal

Medical implants

Corrosion

Metallic-ion release

Surface modification

ABSTRACT

Corrosion prevention in biomaterials has become crucial particularly to overcome inflammation and allergic reactions caused by the biomaterials' implants towards the human body. When these metal implants contacted with fluidic environments such as bloodstream and tissue of the body, most of them became mutually highly antagonistic and subsequently promotes corrosion. Biocompatible implants are typically made up of metallic, ceramic, composite and polymers. The present paper specifically focuses on biocompatible metals which favorably used as implants such as 316L stainless steel, cobalt-chromium-molybdenum, pure titanium and titanium-based alloys. This article also takes a close look at the effect of corrosion towards the implant and human body and the mechanism to improve it. Due to this corrosion delinquent, several surface modification techniques have been used to improve the corrosion behavior of biocompatible metals such as deposition of the coating, development of passivation oxide layer and ion beam surface modification. Apart from that, surface texturing methods such as plasma spraying, chemical etching, blasting, electropolishing, and laser treatment which used to improve corrosion behavior are also discussed in detail. Introduction of surface modifications to biocompatible metals is considered as a "best solution" so far to enhanced corrosion resistance performance; besides achieving superior biocompatibility and promoting osseointegration of biocompatible metals and alloys.

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Contents

1. Introduction	1262
1.1. Metallic biomaterials as implants	1262
1.2. Material selection criteria for implant	1262
2. Corrosion of biocompatible metals	1263
2.1. Types of corrosion in metal implants	1264
2.2. Corrosion: in vitro and in vivo studies	1264
2.3. Effect of corrosion to human body	1265
3. Surface modification to improve corrosion resistance.	1265
3.1. Deposition of coatings	1266
3.2. Passivation-oxide layer	1267
3.3. Ion-beam surface modification	1269
3.4. Surface texturing.	1269
4. Conclusion	1271
Acknowledgement.	1271
References	1271

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1. Introduction

1.1. Metallic biomaterials as implants

The use of metallic biomaterials for biomedical implants has been traced back from the 19th century [1,2]. In recent years, manufacturing and fabrication feature as a primary concern in biomaterial engineering [3–7]. The selection and design of these implants crucially rely on the proposed application [8–11]. The main tenacity in the development of metal-based implant is due to the demands in internal fracture fixation and bone repair. Before the 1860s, metals such as iron, silver, and gold was the primary candidate for bio-metallic devices and used as spinal wires or bone pin [12,13]. The usage of these metals has further dominated other materials in orthopedic surgery since the introduction of Lister's aseptic surgical technique in the 1860s. In orthopedic, depending on the metal implant devices, they are either used as temporary implants (e.g. bone plates, screws, and pins) and permanent implants (e.g. total joints replacement). Recently, there is also increasing trend of using these metal-based implants in the dental and orthodontic applications [3,5,12].

Despite the enormous number of available metals and alloys in the materials industry, only a few metals and alloys can fit the requirements for development as bioimplants. The commonly used metallic biomaterials are 316L stainless steel (316L SS) [14–16], cobalt-based (Co-Cr) alloys [17–20] and titanium and its alloys [2,12,21–24]. Apart of these metals, shape memory alloys such as NiTi [25–27], magnesium (Mg) [28,29] and tantalum (Ta) [12,30,31] which categorized as “miscellaneous material” implants [27,32] are also progressing as a potential candidate. To date, nickel titanium (NiTi) has been used as a vascular stent for non-conventional reconstructive surgery of hard tissues or organs. Where else, magnesium and its alloys showed a bright prospect for application in orthopedic and craniofacial repair [25,29,33]. These are because, Mg exhibits a unique ability to degrade *in vivo* and have similar physical properties as natural bones [28,34,35]. As a result, Mg and its alloys typically used to develop orthopedic fixation plates and screw device. Table 1 shows the primary metallic materials approved for use as a medical implant by the United States Food and Drugs Administration (FDA) and their typical application area in the human body.

1.2. Material selection criteria for implant

The selection of specific metal to be an implant greatly depends on its specific medical application. To serve safely and retainable for a longer period without rejection, these metals should have a few essential properties such as excellent biocompatibility, high corrosion and wear resistance, suitable mechanical properties, osseointegration, ductility and high hardness [2,25,36–38].

Intuitively, the primary essential properties for metallic implant biomaterials to be classified as outstanding candidates for biodegradable medical devices are their innate biocompatibility towards living cells [39–41]. Biocompatibility is defined as the ability of material to be used in close connection with living tissues without causing adverse effects to them [19,42,43]. The body parts or tissue of a patient that comes into contact with the implants should prevent from any physical irritation, inflammation, toxicity, mutagenic, or carcinogenetic action [44–46]. The success of the bioimplants highly depends on the level of compatibility and acceptance of the implant by the human body [47–49]. However, the biocompatibility of implants extremely depends on their corrosion behavior [25,50,51]. Hence, the higher the corrosion of implants, the more of its toxic ions rates are released into the body routinely, and greater risk of adverse effects can be expected [29,52,53].

Human body are made up of a significant number of natural elements with water (H₂O), comprising of about 65 to 75 wt% of the total composition. Accordingly, most of a human body's mass contain oxygen and carbon [12,54]. Table 2 shows a list of elements found in the human body. Where, about 96% of available elements are off oxygen, hydrogen, carbon and nitrogen which are the building blocks of both water and proteins. Additional ~4% of the body mass comes in the form of bone minerals and blood comprising of Ca, P, Mg and extracellular fluids comprising of Na, Cl and K. As such, any implants developed based on these elements would compatible with the human body. However, there are few trace elements which toxic at high levels. Hence, the proper composition required for the metallic implant be free from being toxic. Henceforth the implant will not release toxic metal ions, which causes inflammatory or allergic reactions in the human body.

Furthermore, the bioimplants should possess appropriate mechanical strength to withstand all the related forces and loads. Principally, the selected material for a specific application should have the load withstanding capacity, so they will not be likely to suffer from the fracture [55,56]. Additionally, the implanted biomaterial should be high wear, tear, and corrosion resistance, since they are normally exposed to critical humidity level and high percentage environment that promote localized corrosion surroundings [2,57]. All the considered main criteria discussed above would result in the development of suitable and reliable implant to the human system. However, the current study reveals that most of the bioimplants start to physically fall apart within the period of about 12–15 years. The causes of the failure are due to the chemical, mechanical, surgical, tribological, manufacturing and biocompatibility-related problems [2,57,58].

Among of the critical issues and challenging clinical problem faced today is the failure of an implant due to the corrosion. Despite being naturally occurring, this corrosion resistant biocompatible metal, need to undergo modifications, to enhance their useful properties, especially when used as body implants. The classification of biomaterial for implants are reliant on the main leading features, which are (i)

Table 1
Four classes of metallic biomaterials and their primary applications as implants.

Materials	Applications	Primary utilizations	Applications status	References
Stainless steels	Orthopedic Orthodontic Cardiovascular	Temporary devices (screws, plates and hip nails), total hip replacements	Routinely applied	[12,14–16]
Co-based alloys	Orthopedic Orthodontic Cardiovascular	Total joints replacements, dental implants, removable partial dentures, orthodontic wire leads, femoral stems, bone implant applications, load-bearing implants, bearing surface implant,	Routinely applied	[12,17–20]
Ti-based alloys	Orthopedic Orthodontic Cardiovascular	Dental implants, orthodontic wire leads, cardiovascular, vascular stents, heart valve parts, stem, total hip replacements	Routinely applied	[2,12,21–24]
Miscellaneous				
NiTi	Orthodontic Cardiovascular	Vascular stents, Vena cava filter, Intracranial aneurysm clips, catheter guide wires, orthopedic staples,	FDA approved	[25–27]
Mg	Orthopedic Craniofacial	Biodegradable orthopedic implants	Animal test	[28–32]
Ta		A radiographic marker, wire structures for neurosurgery and plastic surgery	FDA approved	[2,12,33,34]

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