Materials Science and Engineering C 33 (2013) 3563–3575

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Review

A review on nickel-free nitrogen containing austenitic stainless steels for biomedical applications

Mohd Talha, C.K. Behera, O.P. Sinha *

Centre of Advanced Study, Department of Metallurgical Engineering, Indian Institute of Technology (Banaras Hindu University), Varanasi 221005, Uttar Pradesh, India

A R T I C L E I N F O

Article history:
Received 24 June 2012
Received in revised form 30 May 2013
Accepted 4 June 2013
Available online 12 June 2013

Keywords:
Austenitic stainless steel
Biocompatibility
Implant devices
Corrosion

A B S T R A C T

The field of biomaterials has become a vital area, as these materials can enhance the quality and longevity of human life. Metallic materials are often used as biomaterials to replace structural components of the human body. Stainless steels, cobalt–chromium alloys, commercially pure titanium and its alloys are typical metallic biomaterials that are being used for implant devices. Stainless steels have been widely used as biomaterials because of their very low cost as compared to other metallic materials, good mechanical and corrosion resistant properties and adequate biocompatibility. However, the adverse effects of nickel ions being released into the human body have promoted the development of "nickel-free nitrogen containing austenitic stainless steels" for medical applications. Nitrogen not only replaces nickel for austenitic structure stability but also much improves steel properties. Here we review the harmful effects associated with nickel and emphatically the advantages of nitrogen in stainless steel, as well as the development of nickel-free nitrogen containing stainless steels for medical applications. By combining the benefits of stable austenitic structure, high strength, better corrosion and wear resistance and superior biocompatibility in comparison to the currently used austenitic stainless steel (e.g. 316L), the newly developed nickel-free high nitrogen austenitic stainless steel is a reliable substitute for the conventionally used medical stainless steels.

Contents

1. Introduction

Biomaterials are artificial or natural materials, used in the making of structures or implants, to replace the lost or diseased biological structure in order to restore form and function. Thus biomaterial helps in improving the quality of life and longevity of human beings and the field of biomaterials has shown rapid growth to keep up with the demands of an aging population. Biomaterials are used in different parts of the human body such as artificial valves in the heart, stents in blood vessels, and replacement of implants in shoulders, knees, hips, elbows and dental structures [1–3]. Orthopedic

* Corresponding author. Tel.: +91 9452825977; fax: +91 542 2369478.
E-mail address: opsinha.met@itbhu.ac.in (O.P. Sinha).

0928-4931/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.msec.2013.06.002

implant devices are generally mounted on to the skeletal system of the human body for aiding healing, correcting deformities and restoring the lost functions of the original part. Orthopedic implants have improved the quality of life for millions of people over the last quarter of a century [4]. Several metallic materials are used as orthopedic implants in which stainless steels, AISI 316L, are widely employed with its main advantages of low cost, good mechanical properties, easy processing, good corrosion resistance and broader availability. The resistance of these alloys to corrosion is owed to the presence of thin oxide passive film on its surface [5–8]. Although, the resistance to corrosion of stainless steel passive film is relatively high but the passive film is highly susceptible to localized forms of corrosion such as pitting, crevice, and stress corrosion cracking. The most important problem associated with stainless steel is the negative effect of metal ions or fretting debris [9–14], which can be released from the implant devices because of corrosion, wear or other reasons. Considering the potentially detrimental effect of nickel on the human body, experts suggested to restrict the nickel content in the medical stainless steel. Therefore, the nickel-free high-nitrogen austenitic stainless steel (HNS), generally the Fe–Cr–Mn–Mo–N system, has become an important medical metallic material. Nitrogen is a strong austenite forming element and has been successfully used to replace nickel that largely improved the mechanical properties, corrosion resistance and biocompatibility of stainless steels [15,16].

This paper presents an overview of materials for orthopedic applications and their limitations, currently used metallic materials, stainless steels as metallic biomaterials and the problem associated with them, emphatically effect of nitrogen on properties of stainless steels including biocompatibility and development of nitrogen containing stainless steels for biomedical applications.

1.1. Materials for orthopedic applications and their limitations

The materials used for orthopedic implants especially for load bearing applications should possess superior corrosion resistance in the body environment, excellent combination of high strength and low modulus, high fatigue and wear resistance, high ductility and should have no cytotoxicity [17,18]. Materials that are selectively used in orthopedics are ceramics, polymers, composites and metals and alloys. Ceramics are inorganic compounds that can be classified into various categories of biomaterials by their macroscopic surface characteristics or by their chemical stability in the body environment. They are alumina, zirconia, calcium phosphate and bioactive glass (glass ceramics). Alumina and zirconia are mainly used as artificial femoral heads or acetabular liners due to their good mechanical strength and durability in combination with low friction and wear coefficients [19]. Bioactive calcium phosphate ceramics, such as hydroxyapatite (HA) and tricalcium phosphate (TCP, $Ca_3(PO_4)_2$), are mainly used as bone substituting materials [20]. After implantation into the body, HA can form strong chemical bonds with the natural bone and promote new bone growth because of its similar chemical and mineralogical compositions and crystallographic structure to apatite of human bone [21]. However, HA suffers from its brittleness and relatively poor mechanical properties, which impede its clinical use as long term load-bearing applications [22]. Calcium phosphate cements (CPC) are multi-component systems consisting of an inorganic phase and an aqueous solution. The paste or injectable cement is freely moldable and hardens in situ without significant heat development. Potential disadvantages of CPC are relatively poor mechanical properties in relation to bone and lack microporosity, which may hinder tissue in-growth [23]. Bioactive glass mainly consists of sodium, calcium, silicon and phosphorous oxides in various proportions. Bioactivity is mediated by the presence of a hydrated silicate-rich layer, which forms when coming into contact with human fluids. This layer has catalytic effects on the deposition of HA, which in turn leads to a stable bond between glass and bone [24]. These bio-glass formulations show a higher osteogenic potential when compared to HA alone [25]. However, the brittleness and low fracture toughness of bio-glass hampers its use for load-bearing applications.

Polymers are considered for implant applications in various forms such as fibers, textiles, rods and viscous liquids. Examples of biostable synthetic polymers include polymethyl-metacrylate (PMMA), silicone rubber, polyethylene (PE), acrylic resins, polyurethanes or polypropylene. Acrylic bone cements have been used in orthopedic and dental surgeries for many decades to anchor metal or plastic components. However, the use of bone cement does not provide any biological fixation [26]. Recently, polymers have been introduced for hip socket replacement in orthopedic implant applications due to its close resemblance to natural polymeric tissue components. The most commonly used synthetic polymers are poly(α-hydroxyesters), such as PGA, and their copolymers, poly lactic-co-glycolic acid (PLGA) and poly-ε-caprolactone (PCL). However, polymers undergo degradation through bulk erosion and hydrolysis of ester bonds [26]. This results in ionic attack and formation of hydroxyl ions and dissolved oxygen, leading to tissue irritation and decrease in mechanical properties [4]. Degradation rates can be adjusted from weeks to years by modifying the molecular weight, the crystallinity and the co-polymer ratio [27–29]. Composites are materials obtained by combining two or more materials or phases with a view to take advantage of the salient features of each constituent. It is essential that each component of the composite be biocompatible to avoid degradation between interfaces of the constituents. Fiber-reinforced polymers (FRP) are the most widely investigated composites for biomedical applications. Their uncertain lifetimes and degradation under complex states of stress and low mechanical strengths limit their applications. It is also difficult to shape them and they are yet to attain technical maturity for these applications [30].

Metallic materials are most widely used as biomaterials. This is because, when compared to polymeric and ceramic materials, they possess more superior tensile strength, fatigue strength, and fracture toughness [31]. It makes them suitable for load-bearing without leading to large deformations and permanent dimensional changes because of its high strength and yield point coupled with the ductility of metals. Although metals exhibit high strength and toughness, they are susceptible to chemical and electrochemical degradation. The implant materials may corrode and/or wear, leading to the generation of particulate debris, which may in turn aggravate the body environment. The application of metals and alloys is very important in orthopedic, as they play a very predominant role in fulfilling almost every difficult factor that arises in implant applications.

1.2. Currently used metallic implant materials

The fundamental criterion for selecting any implant material is that it should have well biocompatibility. Metals and alloys have been widely used in various forms as implants, which provide the required mechanical strength and reasonable corrosion resistance with good biocompatibility. AISI 316L stainless steels, cobalt–chromium alloys, commercially pure titanium and Ti–6Al–4V alloys are typical metallic biomaterials used for implant devices [32–34]. Some metallic implant materials and their mechanical properties as recommended by ASTM are given in Table 1. These materials are accepted by the body environment because of their passive and inert oxide layer formed on the surface. Austenitic stainless steels are the most widely used material for orthopedic applications. The fabrication and welding of stainless steels is easy as compared to Co–Cr alloys and Ti and its alloys. Stainless steel implants are used as temporary implants to help bone healing, as well as fixed implants such as for artificial joints.

2. Stainless steels as metallic biomaterials

In medicine, the stainless steel which is typically used is austenitic stainless steel (AISI 316L, ASTM F-55 and F-138) which contains