In the Name of God

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Production of nickel-free stainless steel coated with $ZrTiO_4$-PMMA hybrid sol–gel films and investigation of its structure and electrochemical behavior

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PRODUCTION OF NICKEL-FREE STAINLESS STEEL COATED WITH $ZrTiO_4$-PMMA HYBRID SOL–GEL FILMS AND INVESTIGATION OF ITS STRUCTURE AND ELECTROCHEMICAL BEHAVIOR

BY

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Abstract

Production of nickel-free stainless steel coated with $ZrTiO_4$-PMMA hybrid sol–gel films and investigation of its structure and electrochemical behavior

By

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In this research, nickel-free austenitic stainless steels were prepared by mechanical alloying and liquid-phase sintering processes. According to X-ray diffraction and transmission electron microscopy, mechanical alloying of the powder mixture with the chemical composition of ASTM F2581, with iron nitride as the nitrogen source, produced nanocrystalline/amorphous powders. By liquid-phase sintering of the synthesized powder with a Mn-Si eutectic alloy as a novel additive, desirable densification was obtained. Also, X-ray diffraction and transmission electron microscopy showed that the austenite grain size remains yet in the nanometric scale even after the used sintering process at 1050 °C for 60 minutes. The corrosion behavior of the prepared stainless steels was studied by anodic potentiodynamic polarization and electrochemical impedance spectroscopy in a simulated body fluid, suggesting a better resistance compared with AISI 316L. Additionally, human stem cell adhesion evaluations on the synthesized implants confirmed their biocompatibility. In summary, the used mechanical alloying and sintering processes were found to be worthy to prepare nanostructured stainless steels with a high relative density and a desirable corrosion and cytocompatibility behavior. Afterwards, to improve the corrosion resistance and biocompatibility of the substrate, two types of sol–gel

derived thin films ($ZrTiO_4$ and hybrid $ZrTiO_4$–PMMA) were deposited by a spin coating method. In the used particulate sol–gel process, a polymeric dispersant, namely carboxymethyl cellulose, was originally used to avoid agglomeration of nanoparticles and to obtain desirable film qualities. The films were characterized by differential scanning calorimetery, X-ray diffraction, transmission electron microscopy, atomic force microscopy, and scanning electron microscopy, indicating the preparation of high-coverage, crack-free, and homogeneous coatings. Water contact angle, electrochemical, and biocompatibility evaluations demonstrated that the coatings improve the hydrophilicity, corrosion resistance, and thereby biocompatibility of the substrate. Despite the higher corrosion protection by the hybrid $ZrTiO_4$–PMMA coating, the sample coated with the pure $ZrTiO_4$ thin film exhibited a better cell viability. Furthermore, a new double-layer sol–gel coating, which comprises $ZrTiO_4$ as the bottom layer and $ZrTiO_4$–PMMA as the top layer, was deposited on the stainless steel substrate. According to potentiodynamic polarization experiments, the substrate coated with this new film exhibited superior corrosion resistance, compared with the same steel coated with purely inorganic $ZrTiO_4$ and hybrid $ZrTiO_4$–PMMA films. In summary, the $ZrTiO_4$-based sol–gel films can be considered as an efficient approach to improving the corrosion resistance and biocompatibility of metallic implants.

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Chapter 1

Introduction

1. Introduction

Metals and alloys are the oldest materials used in surgical purposes to make devices for fracture fixation, joint replacement, external splints, braces, and traction apparatus, as well as dental amalgams. Nowadays, the widely used metallic biomaterials include stainless steels, titanium and its alloys, cobalt-chromium-based alloys, as well as tantalum, niobium, and gold. Stainless steels, typically AISI 316L, are conventionally used in orthopedics, with main advantages of low cost, good mechanical properties, sufficient corrosion resistance, and easy processing. However, problems have been found with this type of medical-grade stainless steels. The most important problem is the negative effect of metal ions or fretting debris released from the implant due to corrosion and wear. Nickel and chromium are known as potentially harmful elements in the medical stainless steels. Nickel ions act as allergens in the human body, which may cause inflammations like swelling, reddening, eczema, and itching on skins. Due to the harmful effect of nickel ions on the human body, nickel-free austenitic stainless steels, generally Fe–Cr–Mn–Mo–N system, are considered as a potential replacement for conventional nickel-containing alloys. Because of this, with the development of new surgical stainless steels and the modification of ASTM medical standards, the nickel content is decreasing and the nitrogen content is increasing. Currently, in ASTM standards, two nickel-free medical-grade stainless steels are pointed out: ASTM F2229 and ASTM F2581.

To produce nitrogen-containing nickel-free austenitic stainless steels, there are several methods, such as melting processes, solid nitrogen absorption treatment, and powder metallurgy. It is known that mechanical alloying is a capable process to synthesize a wide variety of equilibrium and non-equilibrium structures, including supersaturated, metastable crystalline, quasicrystalline, intermetallic,

nanostructured, and amorphous alloy powders. This powder processing route can be successfully used to produce nitrogen-containing stainless steels. Nitrogen alloying through mechanical alloying can be accomplished by either milling under a reactive nitrogen atmosphere or milling under an inert atmosphere with metal nitrides. On the other hand, to meet the best mechanical and corrosion behaviors of powder metallurgy parts, high densities are imperative. To do so, a number of approaches like warm compaction, increasing sintering temperature and time, and using proper additives to activate liquid-phase sintering are under consideration. In the liquid-phase sintering process, the formation of a liquid phase promotes densification via providing a particle rearrangement, faster diffusion rate, and pore elimination.

In the biomaterials field, as well as the modification of the chemical composition of stainless steels, leading to the development of nitrogen-containing nickel-free alloys, surface modification techniques are considered, with the principal purpose of an improvement in corrosion resistance, wear resistance, antibacterial property, and tissue compatibility. Coating, as one of these methods, not only can increase the corrosion resistance of the implant, but also can improve the implant-tissue interaction, affecting biological responses like bioactivity and cytocompatibility. Among various methods used to process coatings, the sol–gel deposition process has advantages, such as high homogeneity, low sintering temperatures, and simplicity of complex shape coating.

In this thesis, medical-grade stainless steel powders with the nominal composition of ASTM F2581 were prepared by mechanical alloying. After powder characterization, bulk stainless steel samples were prepared by liquid-phase sintering of the same mechanically-alloyed powder with a Mn-Si eutectic alloy. Also, the corrosion behavior and cytocompatibility (stem cell adhesion) of the prepared samples were evaluated. Then, two types of sol–gel derived coatings ($ZrTiO_4$ and $ZrTiO_4$–PMMA) were deposited on the stainless steel sample, to improve corrosion resistance and biocompatibility. Zirconium titanate ($ZrTiO_4$) and polymethyl methacrylate (PMMA) are known as a biocompatible ceramic and polymer, respectively. The

electrochemical behavior and cytocompatibility of the coated samples were also evaluated. Finally, the cell adhesion to the samples was correlated with surface characteristics of roughness, wettability, and corrosion resistance.

Chapter 2

Theory and literature review

2. Theory and literature review

2.1. Biomaterials

2.1.1. An introduction to biomaterials

Williams [1] defined biomaterials as “nonviable materials used in medical devices, intended to interact with the biological systems”. The basic requirement of a biomaterial is that the material and tissue environment should coexist without any undesirable effect on each other, defined as biocompatibility. These devices are termed as “implants” when they are intended to remain there for a substantial period, and as “prosthesis” when they are permanently fixed in the body for a long-term application until the end of lifetime [2]. Fig. 2-1 summarizes applications of inorganic biomaterials in the musculoskeletal system of the human body.

Orthopedic devices are generally implanted into the skeletal system of the human body for healing, correcting deformities, and restoring the lost functions of the original part. They are supporting bone plates, screws, total hip joints, knee joints, elbow joints, shoulder joints, and reattachments for tendons or ligaments. The implants are exposed to the biochemical and dynamic environment of the human body and their design is dictated by anatomy and restricted by physiological conditions. In the past few decades, the increase in the utilization of self-operating machines, participation of many persons in sports, defense activities, increased interest in motorcycles and bicycles, and day-to-day increasing traffic, have resulted in an enormous increase in the number of accidents. This has automatically led people to refer to orthopedic implants for the early recovery and resumption of their routine activities, which has provided a high level of motivation for the further development of orthopedic implants [3].

2.1.2. Metallic biomaterials

Metals and alloys are the oldest materials used in surgical purposes to make devices for fracture fixation, joint replacement, external splints, braces, and traction apparatus, as well as dental amalgams [3]. Because metals and alloys, compared to polymers and ceramics, have a more tensile strength, fatigue strength, and fracture toughness. Because of the critical and detrimental effects of corrosion on the human body, the history of metallic implants development has been mainly focused on better corrosion-resistant materials.

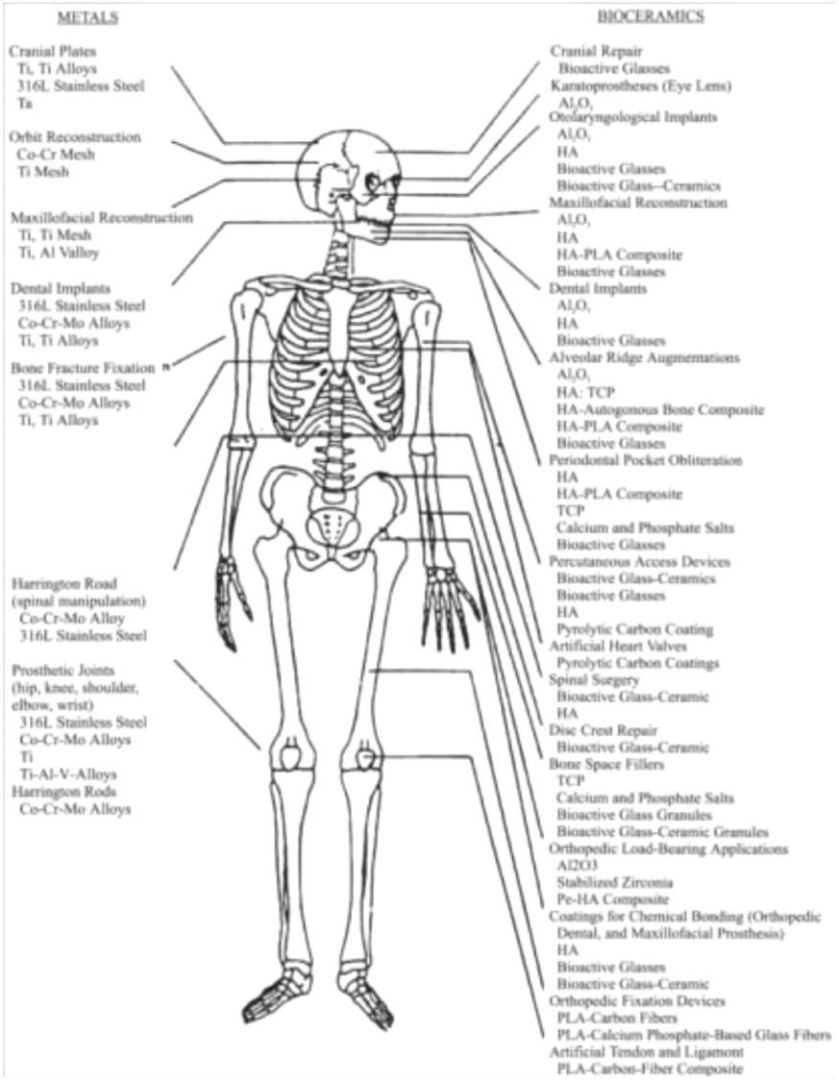

Fig. 2-1. Clinical uses of inorganic biomaterials [3].