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Bio-corrosion behavior and mechanical characteristics of magnesium-titania-hydroxyapatite nanocomposites coated by magnesium-oxide flakes and silicon for use as resorbable bone fixation material

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ABSTRACT

This study was aimed to improve of the corrosion resistance and mechanical properties of $Mg/15TiO_2/5HA$ nanocomposite by silicon and magnesium oxide coatings prepared using a powder metallurgy method. The phase evolution, chemical composition, microstructure and mechanical properties of uncoated and coated samples were characterized. Electrochemical and immersion tests used to investigate the in vitro corrosion behavior of the fabricated samples. The adhesion strength of ~36 MPa for MgO and ~32 MPa for Si/MgO coatings to substrate was measured by adhesion test. Fabrication a homogenous double layer coating with uniform thicknesses consisting micro-sized particles of Si as outer layer and flake-like particles of MgO as the inner layer on the surface of $Mg/15TiO_2/5HA$ nanocomposite caused the corrosion resistance and ductility increased whereas the ultimate compressive stress decreased. However, after immersion in SBF solution, Si/MgO-coated sample indicates the best mechanical properties compared to those of the uncoated and MgO-coated samples. The increase of cell viability percentage of the normal human osteoblast (NHOst) cells indicates the improvement in biocompatibility of $Mg/15TiO_2/5HA$ nanocomposite by Si/MgO coating.

1. Introduction

Design of novel materials for orthopedic applications with in situ degradability characteristic in physiological environment is aim of extensive researches in the last years (Meischel et al., 2016; Mostaed et al., 2016). Due to the ability of magnesium to solve the biodegradability, stress shielding and osteocompatibility problems, as well as the similar mechanical properties to human bone, it attracted a lot of interest as a replacement orthopedic implant materials to clinical applications over other traditional metallic materials (Dezfuli et al., 2017; Del Campo et al., 2017; Rosalbino et al., 2010; Song, 2007; Wolf and Cittadini, 2003; Nayak et al., 2016; Zhang et al., 2010; Zheng et al., 2014). However, because of the high degradation rate of magnesium in living body environment, the magnesium-based implant lost its mechanical strength before healing of the injured tissue, which could not afford effective biomechanical support and match the bone reconstruction (Ibrahim et al., 2017; Zhang et al., 2016a). In addition to the high corrosion rate, the low bioactivity of magnesium implants as the ability to form hydroxyapatite (HA) is another challenging problem, which need to be resolved before utilization in clinical applications (Chen et al., 2015). To overcome this drawback, several surface modification techniques, i.e. electrochemical deposition (Liu et al., 2012; Mohedano et al., 2015), polymer treatment (Qi et al., 2016; Zomorodian et al., 2013), chemical deposition (Lin et al., 2016; Lu et al., 2012), and micro-arc oxidation (MAO) techniques (Gu et al., 2011; Krishna et al., 2015; Lin et al., 2013), have been introduced to improve the degradation rate and bioactivity of magnesium and its alloys. As is known, fabrication of magnesium-based composites with

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bio-ceramic additives (Khalajabadi et al., 2017), besides the surface modification of magnesium implants, and alloying magnesium with biocompatible metals (Fintova et al., 2015; Shi et al., 2015a, 2015b) are the major techniques to protect the implant from fast corrosion and degradation in vivo. Moreover, bio-additives and suitable coatings can improve the hemocompatibility and bioactivity of implants in this field (Heublein et al., 2003; Li et al., 2010; Paital and Dahotre, 2009; Zartner et al., 2007). Gu et al. reported that pure Mg as the matrix materials, and HA as the bio-ceramic additive, were selected to fabricate the Mg/HA biocomposite with different amount of HA content using the powder metallurgy (PM) route. The cytotoxicity tests indicated that Mg/10HA extract showed no toxicity to L-929 cells (Gu et al., 2010).

In our previous work, magnesium-matrix composites with titania and hydroxyapatite reinforcements were developed, as well as an enhancement in degradation resistance and mechanical properties was achieved by addition titania. According to the cell culture results, the Mg/15TiO_2/5HA nanocomposite was biocompatible with osteoblasts (Khalajabadi et al., 2016). As was reported by Li et al., the silicon coating was deposited on the surface of WE43 Mg alloy using PECVD technique to slow down its degradation rate for medical application (Li et al., 2013). Moreover, the corrosion resistance and mechanical properties of Mg/HA/TiO_2/MgO nanocomposites were enhanced by Si mono-layer and Si/ZnO double layer coatings that were fabricated using Radio Frequency Magnetron Sputtering technique (Khalajabadi et al., 2015). Silicon (Si), as an essential mineral in human bodies, is substituted alone or in combination with a variety of other materials for filling bone defects (Khan et al., 2014). In the early stage of bone calcification, silicon was involved according to the reports of Carlisle (Carlisle 1970) and Schwarz and Milne (Schwarz and Milne 1972). Moreover, the stimulation of cell proliferation by Mg and Si ionic products was found by Wu and Chang (Wu and Chang, 2007). It has been concluded that Si plays a significant role in bone repair and regeneration of bone. Therefore, the in vivo biological performance of the Mg alloy should be enhanced using Si-containing coating (Wang et al., 2015b). In addition, the anticorrosion ability and hemocompatibility of Mg alloy for biomedical application has been significantly improved by MgO coating synthesized using micro-arc oxidation in a multi-step surface modification process. A porous MgO coating as an intermediate layer was prepared on the surface of AZ31 magnesium alloy to the improvement of corrosion resistance (Shi et al., 2015a, 2015b). Brink (Brink, 1997) added MgO to a series of bioactive glasses to maintain bioactivity. Some in vitro results actually indicate that MgO has a detrimental effect on apatite formation (Ebisawa et al., 1990; Kasuga et al., 1987; Watts et al., 2010). Furthermore, (Oliveira et al., 2000) claimed that MgO has a beneficial effect as it improves the early stages of mineralization and contributes to intimate contact with living tissue.

In present study, a powder metallurgy technique consisting of ball milling–multi step cold pressing and subsequent sintering used for fabrication monolayer MgO and double-layer Si/MgO coatings on the surface of Mg/15 wt%TiO_2/5 wt%HA nonocomposite to enhance the corrosion resistance, mechanical integrity and biocompatibility of this nanocomposite for implant applications. Therefore, microstructure, in vitro biocompatibility, mechanical properties, electrochemical and long-term corrosion behavior of uncoated and coated nanocomposites were investigated.

2. Materials and methods

2.1. Preparation of the powder samples of uncoated, MgO-coated and Si/MgO-coated Mg/TiO_2/HA bionanocomposites

2.1.1. Raw materials

Pure magnesium powder (Mg powders, ≥ 99%, 5–20 μm particle size), periclase nanopowders (MgO, 99%, average particle size < 100 nm), hydroxyapatite (HA nanopowder ≥ 97%, < 100 nm particle size), and pure Si (99%, sieve size of 325 mesh) powders under SIGMA-ALDRICH brand used as the raw materials.

2.1.2. Preparation of the uncoated Mg/TiO_2/HA bionanocomposites

A vacuum dry oven used to dry the raw material and the coating powders (Si powders and MgO with flake-like morphology) at 220 °C for 10 h. A subsequent mixing by a planetary ball mill was performed on the 80 wt% Mg, 5 wt% HA and 15 wt% TiO_2 powders in an inert gas atmosphere for 2 h. A uniaxial press at ~840 MPa pressure used to fabricate of cylindrical pellets (Ø12 mm × 5 mm) of uncoated Mg/15TiO_2/5HA bionanocomposites from ball-milled powders. Subsequently, the pellets sintered for 2 h at ~400 °C in a tube furnace under argon atmosphere to finish the fabrication process of compact bare specimens.

2.1.3. Preparation of the MgO-coated Mg/TiO_2/HA bionanocomposites

For preparation of MgO-coated samples, the ball milled powders of Mg, HA and TiO_2 mixture pressed at pressure ~460 MPa in first stage of cold pressing. Then as illustrated in Fig. 1, the upper punch exited from the steel die and a specific amount of MgO powders (consisted of sheet-like particles) decanted on the surface of cold-pressed nanocomposite inside the die. After decanting the MgO powders on the surface of pressed sample that were inside the steel die, a vibration system used to homogenize the thickness of MgO powders in different places of surface of the pressed nanocomposite. In next stage, cold pressing was applied at ~815 MPa to assemble of MgO coating on the surface of Mg/TiO_2/HA nanocomposite. The amount of added MgO in steel die was determined by repeating the experiments, SEM microscopy observations of thickness of MgO coating, density measurements and the coating adhesion measurements to obtain the acceptable adhesion strength of fabricated MgO coating layer with substrate. The minimum required value for the adhesion strength of coatings to the implants is 22 MPa, according to ASTM1147-F (Shi et al., 2015a, 2015b). In last stage, the MgO-coated sample sintered for 1.5 h under argon atmosphere.

2.1.4. Preparation of the Si/MgO-coated Mg/TiO_2/HA bionanocomposites

In the case double layer Si/MgO coating, the cold pressing performed at 340 MPa to press ball-milled Mg/TiO_2/HA powders and 570 MPa pressure was applied to fabricate MgO layer on the surface of cold-pressed Mg/TiO_2/HA in first and second stages of pressing, respectively. In the third step, the specific amount of Si powders decanted on the surface MgO-coated sample into the die, the thickness of Si layer homogenized in different parts of surface using vibration system, and then the powder system pressed under around 800 MPa pressure. As reported in MgO coating process, the amount of Si powder for coating was determined by repeating coating process to obtain the fabricated coatings with good adhesion strength to substrate that is very important factor to protect Mg-substrate implants against corrosive solution. Finally, the Si/MgO-coated nanocomposite sintered 2 h at 540 °C under argon atmosphere for densification of powder sample and better adhesion coating to the substrate. The characterization, corrosion investigations, mechanical analysis and biological tests performed on these sintered pellets. The relative density (=measured density/theoretical density) of the sintered pellets considered as an important parameter to determine the cold pressing and sintering condition, as the minimum ratio of relative density was 85% to carry out a reasonable comparison in corrosion resistance, mechanical characteristics and cytotoxicity uncoated and coated Mg/TiO_2/HA bionanocomposites.

2.2. Characterization of the powder samples of uncoated, MgO-coated and Si/MgO-coated Mg/TiO_2/HA bionanocomposites

The surface and cross-sectional morphologies of the coatings, as well as the corrosion products were observed using a field-emission scanning electron microscopy (FE-SEM) and a transmission electron microscopy (TEM). The crystal structure, phase evolution and chemical