



Effect of mechanical alloying on the phase evolution, microstructure and bio-corrosion properties of a Mg/HA/TiO₂/MgO nanocomposite

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Abstract

In this study, a magnesium-matrix nanocomposite comprising bioactive ceramics of Mg-substituted hydroxyapatite (HA), farringtonite (Mg₃(PO₄)₂), perovskite (CaTiO₃), geikielite (MgTiO₃) and brucite (Mg(OH)₂) was synthesised through mechanical alloying and annealing of a Mg–HA–TiO₂–MgO mixture by mechanically induced self-propagating reactions. The phase evolution and microstructure were analysed using X-ray diffraction, field-emission scanning electron microscopy and transmission electron microscopy. The results indicated that after 16 h of milling, the powder mixture exhibited a homogenous distribution of fine agglomerates composed of spherical particles with an average size of 83 nm. The crystallinity and thermal stability of the HA phase decreased with increasing milling time because of the substitution of Mg atoms in the HA structure. The mean crystallite size of the product phases was approximately 75 nm after 8 h of mechanical alloying, and these values increased slightly to 82 and 88 nm after 1 h of annealing at 500 and 630 °C, respectively. The bio-corrosion properties of the nanocomposites were investigated using electrochemical tests and immersion tests after different milling times and subsequent annealing. The electrochemical tests revealed that the corrosion potential (E_{corr}) of the as-blended samples shifted towards a nobler direction from –1565 to –1457 mV_{SCE} by increasing the amount of HA from 12.5 wt% to 25 wt%. After 16 h of milling, the corrosion resistance of the milled samples comprising 12.5 wt% and 25 wt% HA increased to 4.63 and 4.97 kΩ cm², respectively. The milled samples annealed at 630 °C exhibited lower corrosion rates compared with those annealed at 500 °C. The present study suggests that the high-energy ball milling of the Mg–HA–TiO₂–MgO mixture accompanied with post annealing is a promising option for controlling the rapid corrosion rate.

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1. Introduction

In recent years, the biocompatibility and biodegradability of magnesium and its alloys have led to significant attention regarding orthopaedic applications of these alloys [1–4]. Stress-shielding effects are minimised using Mg alloys as implants because their Young's moduli (approximately 45 GPa) are similar to that of human bone (10–15 GPa) [1,2,5]. Non-toxicity and

good bone cell adhesion are two other significant characteristics of Mg alloys [3,5]. However, their rapid degradation in simulated body fluid (SBF) is a major drawback, which results in the alloy losing mechanical integrity before the injured tissues have had sufficient time to heal. This phenomenon also leads to the release of hydrogen gas and the alkalisation of body fluid [6]. Hence, one of the principal requirements for using magnesium as a bio degradable implant is the improvement of its corrosion resistance. Three effective routes, alloying [3,4,6], surface modification [7,8] and the formation of magnesium-matrix biocomposites reinforced with bioactive ceramics [9,10], have been applied to reduce the

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degradation rate of magnesium. Powder metallurgy routes such as mechanical alloying (MA) are a promising method with which to fabricate Mg/bioceramic composites. MA is a solid-state reaction for producing various non-equilibrium phases or alloys, such as amorphous phases, supersaturated solid solutions, nanostructured materials and nanocomposites in powder form [11–16]. MA leads to an improvement in the mechanical properties of Mg-based biocomposites by refining the grain size compared with the as-cast Mg samples containing larger grains and a preparation of a homogenous dispersion of reinforcement particles [17,18]. It is well known that HA and TiO₂ are biomaterials with stable and osteoconductive properties [9,10,19]. Furthermore, the presence of HA and CaTiO₃ in implants clearly enhances the bioactivity of the implants for biomedical applications [20,21]. As previously reported, periclase (MgO) is a degradable component that exhibits antibacterial properties [22]. The formation of dense corrosive products of Mg(OH)₂ plays an essential role in reducing the degradation rate of Mg alloys [23]. Moreover, there have been numerous investigative reports on the substitution of Mg in the HA structure because of its potential to improve artificial bone and to develop other medical applications [7]. According to the literature, the deposition of an Mg₃(PO₄)₂ and magnesium phosphate composite (MgP) on the surface of Mg alloys improves corrosion resistance, provides positive bone regeneration stimulation and increases the mechanical strength of Mg alloys. MgP can be combined with calcium phosphate components to modify the biological performances of the final products [24–27]. Moreover, the biocompatibility and osteoconductivity of magnesium titanate oxide (MgTiO₃) as an implant for use in biomedical fields was reported by Sul [28]. Thus, the presence of geikielite (MgTiO₃) and periclase (MgO) phases accompanied with HA in outputs can improve the mechanical and biological properties of calcium-phosphate-based materials [28,29]. Therefore, in this study, magnesium (Mg), hydroxyapatite (HA), titanium dioxide (TiO₂) and magnesium oxide (MgO) are used as raw materials for the synthesis of an Mg–HA–TiO₂-based nanocomposite by MA. The mechanochemical synthesis of this nanocomposite and the formation mechanism of the composite nano-powders were investigated. However, Mg-substituted HA, Mg₃(PO₄)₂, CaTiO₃, MgTiO₃ and Mg(OH)₂ phases, through MA and post-annealing processes, have not been reported elsewhere. In addition, the bio-corrosion properties, morphological characteristics and phase evolution during MA and thermal annealing were also investigated.

2. Materials and methods

2.1. Preparation of powder samples

Pure magnesium powder (Mg, 99.9%, 325 mesh), hydroxyapatite (HA, average particle size < 1 μm), anatase (TiO₂, with tetragonal structure, average particle size < 1 μm) and periclase (MgO, average particle size < 1 μm) supplied by SIGMA-ALDRICH were used as the starting materials. Powder mixtures of two compositions: 67.5Mg–12.5HA–10TiO₂–10MgO (wt%) and 55Mg–25HA–10TiO₂–10MgO (wt%), named samples MHT1 and MHT2, respectively, were

dried in a vacuum dry oven at 220 °C for 10 h. The mechanochemical process was performed using a Retsch pm 100 planetary ball mill in a polyamide-vial (volume of 125 ml) using zirconia balls for 2, 4, 8 and 16 h under an argon atmosphere. The details of the ball-milling conditions are presented in Table 1. Subsequent annealing of the mechanically activated powders was performed in a tube furnace at 500 and 630 °C for 1 h under an argon atmosphere. The annealing process was fixed at a heating rate of 15 °C/min from room temperature to the desired temperature.

2.2. Characterisation of powder samples

X-ray diffraction (XRD) was used in the phase analysis of the milled and annealed powder samples. A Philips diffractometer (40 kV, 30 mA, step size 0.05 degree and time per step of 1 s) with Cu Kα radiation (λ=0.15406 nm) was used for the XRD measurements. The analysis of the XRD patterns was performed using “MDI jade6” software. The XRD patterns were compared with standards compiled by the JCPDS standards. The crystallite size was determined using the Williamson–Hall method [30] according to the following equation:

$$\frac{\beta}{2} \cot \theta = \frac{0.45\lambda}{\sin \theta D} + \epsilon \quad (1)$$

where β is the diffraction peak width at mid-height, λ is the X-ray wavelength, D is the average crystallite size (nm), ε is the micro-strain and θ is the Bragg diffraction angle. The crystallite size of the powder mixture was calculated using the maximum reflections of each of the raw materials and product phases, from which an average value was reported as the crystallite size. Moreover, the following relation between the lattice spacing (d) and lattice parameters (a, b and c) of the HA phase was used [31]

$$\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \quad (2)$$

where h, k, l are the Miller indices of the reflection planes. The lattice parameters were calculated by selected reflections of (002) and (300) of the HA phase. In addition, the calculated values of the HA lattice parameters using Eq. (2) was confirmed by the “MDI jade6” software. The following equation was used to determine the fraction of crystalline

Table 1
Mechanical alloying parameters adopted for milling Mg-HA-TiO₂-MgO powder samples.

| Parameter | Value |
|----------------------------|------------------------|
| Rotation speed (rpm) | 300 |
| Ball-powder weight ratio | 20:1 |
| Vial and ball material | Polyamide and Zirconia |
| Diameter of the balls (mm) | 5 and 10 |
| Mass of the balls (g) | 3 and 24 |
| Mass of powder (g) | 10 |
| Capacity of vial (ml) | 125 |

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