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Synthesis and characterization of Mg-Zn-Mn-HA composite by spark plasma sintering process for orthopedic applications

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ABSTRACT

This paper presents an investigation of design and development of low elastic modulus porous biodegradable Mg-Zn-Mn-HA composite for orthopedic applications via mechanical alloying and spark plasma sintering (MA-SPS) technique. The effect of MA-SPS process parameters like milling time, sintering temperature and sintering pressure have been studied on the structural porosity, elastic modulus and hardness of as-synthesized composite. The percentage of structural porosity was determined by Archimedes method and the elastic modulus and hardness of as-synthesized alloy were measured by the nano-indentation method. HA compound induced composite not only refined the grain but also enhanced porosity, which favoured osseointergation. The microstructure examination of the MA-SPS synthesized composite reveals the formation of high degree of structural porosity (15–25%), witnessed at low alloying time and high temperature. Sintering pressure enables pores reduction and induces an additional driving force for the compaction and sintering temperature assists the powder particles to coalesce, which subsequently reduces the porosity, densified the compact, and enhanced the mechanical properties. XRD pattern analysis confirmed the formation of MgCaO, β-TCP, Mn-CaO, and Ca-Mg-Zn phases, enhanced mechanical properties and corrosion characteristics. The degradation rate of Mg-Zn-Mn-HA alloy was reduced from 1.98 mm/year to 0.97mm/year by the alloying of HA elements.

1. Introduction

The increased demand for an artificial organ, hard tissue replacement, and bone fixation devices led to the evolution of the wide range of newer biomaterials [1–3]. The common and successful in the class of metallic implants are stainless steel, cobalt-chromium, titanium [4–9]. The bio-implants which are used as a bone fixation devices needs to remove from the body after healing by a secondary surgical procedure, thus causing an increased healthcare cost, and mental stress towards the patients [10–17]. In light of this concerns the existing hard metallic implants, magnesium (Mg) based alloys/composites are gaining a growing attention as a promising alternative for the developments of bio-inserts and bone fixation devices among all bio-materials, because of their high biodegradability, superior biocompatibility and low elastic modulus nearing to that of the bone [18]. However, the major drawback of Mg, which limits its eminent use in medical applications, is the fast degradation after implantation [19]. Over the decades, numerous methodology and progressive techniques have been employed to regulate the deterioration rate in a way such that the implant provides adequate mechanical integrity until the complete bone healing [20–22]. This has been a pressing challenge for biomedical engineers and material scientists are aiming to explore the inherent solutions to produce implants with the controlled degradation ability [23]. The alloying elements in Mg matrix were found the most successful and latent method to control the degradation rate of Mg composites [24]. Progressively in this direction, several magnesium alloys/composites have been synthesized by different alloying elements such as Mn [19], Zn [19,20], Li [21], Al [22], Si [22], Sn [23], Dy-Sr-Nd-Zr [24], Y [25,26], Ni [26], and Nd [25,26] have been used to enhance Mg-alloy corrosion resistance.

Recently, the spark Plasma Sintering (SPS) has been accounted for a flexible and potential candidate to fabricate metallic and ceramic alloys and composites with improved mechano-biological properties and corrosion characteristic [27]. The SPS technique was used for the fabrication of porous implants by optimizing its process parameters. The fabricated porous implant possessed desired bio-mechanical integrity required for the orthopedic applications [28]. Gua et al. reported the application of SPS technique to fabricate the Mg/nano-HA alloy. The

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effect of nano-HA wt. % on the mechano-corrosion characteristics was studied and observed that Mg-10 wt% nano-HA alloy possessed the superior corrosion resistance properties. The alloying elements, HA element have extraordinary integration of mechano-biological antibacterial and corrosion properties. Moreover, element HA is a main and prime part of the human bone that can stimulate the bone ingrowth process [29]. Singh et al. reported the synthesis and development of biomimetic biodegradable Mg-alloys using Zn, Mn, and HA element through MA-SPS technique. The fabricated alloy possessed maximum microhardness of 97 HV, which comparatively higher than that of values of conventional Mg alloys. Alloying of HA in combination with Mn and Zn not only refines the grain structure but also improved the biomechano-corrosion properties [30]. The alloying of Mn and Zn in Mg matrix was investigated [31,32]. The study showed that Mg-Zn-Mn alloys are biodegradable in human body environment without causing sediments in the tissues' localities and the biodegradability of as-fabricated alloys were improved with the addition of HA. The addition of Mn and Zn controls the deterioration rate of the Mg alloys and improved the stability of implant material. Fu et al. fabricated Mg-Zn-Mn-Ca alloys by SPS technique, which exhibits yield strength of 58–69 MPa, Tensile strength 177–205 MPa, and hardness 49–53 Hv [33]. Rudinsky et al. fabricated high hardness and high flexural strength (~659 MPa) Al–Zn–Mg alloy by SPS technique [34]. Cao et al. fabricated Mg-ZnO by SPS technique and the findings suggested that as fabricated Mg-10 wt % ZnO composite has excellent bio-corrosion resistance properties and potential candidate for temporary implant application [35]. Moreover, the ZnO powder enhanced the strength and the ductility of the fabricated composites. Narita et al. fabricated high densified Mg/β-TCP composites of excellent mechanical properties and high hardness [36].

Till date, numerous researcher studies are available on the fabrication of Mg-alloy alloyed with Mn, Zn, Si, HA, TCP and thereby combinations via different methodologies. However, based on the best knowledge of the authors, very few emphasized the effect of process parameters of SPS technique on quality characteristics of sintered alloys and composites. In the present study, the effect of process parameters on the quality characteristics such as structural porosity and elastic modulus of MA assisted SPS biodegradable porous Mg-Zn-Mn-HA alloy was attempted, which provides the insight into the design and development of Mg-based implant alloys.

2. Materials and method

The constituent such as Mg, Mn, Zn, and HA of high purity (~99.9%) was used to prepare Mg-Zn-Mn-HA alloy. The wt% of HA powder is considered as a process parameter while fabricating Mg alloy, as presented in Table 1. The composition constituents (in mass fraction) were mixed and mechanically alloyed in a high energy planetary ball mill (*make*: Fritsch, Pulverisette-7) by using stainless steel vial and balls. The as-blended powder mixture was first pre-heated at 200 °C for 2 h in an argon atmosphere (1 l/min) to evaporate the moisture and further consolidated via spark plasma sintering (SPS) technique using a SPS-5000 machine (Model: Dr. Sinter SPS-625, Fuji Electronic Industrial Co. Ltd., Japan) in a graphite die at the heating rate of 50 K/min (holding time 15 min) under vacuum conditions with different sintering temperatures and uniaxial pressure. A circular compact with diameter 20 mm and thickness 5 mm were prepared. From the pilot experimentations and available literature, four process parameters such as: milling/alloying time (T_m), sintering temperature (T_s) and pressure (P_s)] were selected as presented in Table 1.

Table 1
Process parameter of MA-SPS process and their level.

Process parameters	Symbol	Units	Levels
HA wt.%	HA	%	0, 10, 20
Milling time, h	T_m	hrs	4, 8, 12
Sintering pressure	P_s	MPa	10, 20, 40
Sintering temperature	T_s	K	300, 350, 400
Heating rate		K/min	50
holding time		min	5
Atmosphere			Argon

The elastic modulus (Y_m), and hardness (HV) of MA-SPS fabricate Mg-Zn-Mn-HA alloys were chosen as output response characteristics. The microstructure, surface morphology, and element composition of the as-prepared samples were characterized by field-emission scanning electron microscopy (*make*: FE-SEM; JEOL 7600F) coupled with energy dispersive spectroscopy (EDS). The specimens were polished appropriately to analyze the microstructure. The phase formation was examined by X-ray diffraction (*make:* XRD; X'pert-PRO, PAN analytical, Almelo, The Netherlands). The samples were scanned at incident angle over a 2θ range of 10–80° using CuKα radiation operating at 45 kV and 40 mA. The micro-hardness of the coating was measured by Vickers hardness tester (*make*: HMV-G21ST, SHIMADZU, Japan) as per the procedure adopted in previous research.

The percentage of structural porosity was calculated by Archimedes method using water. First samples' mass was weighed and then immersed in the small beaker. The weight of the sample in water was measured, whereby the loss of weight of the sample when suspended in water was equal to the mass of fluid displaced, from which its volume and hence open porosity could be calculated using formula:

$$P = (1 - m/v*\rho)*100$$

The Young's modulus is the basic characteristics of the biomaterial and is of the interest to determine mechano-biological stability. Thus, elastic modulus and hardness were determined via nanoindentation tests (make: Hyistron TI-950 indentation system) using the Oliver-Pharr method, as reported by Oliver et al. [37]. The Berkovich tip was used for the indentation with a maximum applied load of 1000 μN intensity. The corrosion behavior were assessed via electrochemical potentiodynamic workstation (DC potentiostat/galvanostat model, Auto Lab PGSTAT30, Netherlands). To mimic the human body fluid condition, Ringer's solution as a SBF (simulated body fluid) was used as an electrolyte. The polarization behavior was monitored after 24 h immersion the specimens in SBF with the scan rate of 0.001 V^{-1}. Three-electrode cell was utilized equipped with the specimen as a working electrode, the graphite rod as a counter electrode, and Ag/AgCl saturated calomel as a reference electrode. The corrosion parameters were determined from the Tafel plot using Stern-Geary, as per ASTM standard G102-89, as per the procedure adopted by Prakash et al. [38]. The degradation rate of the as-fabricated composites was assessed by the immersion test in SBF solution for 3, 7, and 14 days, as per procedure reported in ASTM-G31-72 standard [39].

3. Results and discussions

3.1. Mechanical alloying

The net weight of powder mixture before and after mechanical alloying was approximately 10 g m, which clearly indicates that there is no loss of powder. The change in particle size and morphology is a function of milling time. After milling for 12 h, the powder particulate reduced in size notably and becomes irregular in shape. The reduction in grain size was due to plastic deformation and fragmentation in milling. After milling, the powder particles were completely homogenized, as can be seen in Fig. 1 **(a)**. Furthermore, it was observed that the powder particles were not defused with each other due to the raised localized temperature for the extended time period. Zheng et al. reported similar finding when Mg particles were milled with Al and Cu for more than 10 h [40]. The grain size and the lattice strain of the milled powders were calculated using Hall-Williamson method [41]. Fig. 1 (b) shows that the grain size decreased whereas the lattice strain increased, as the milling time increased. The average grain size and lattice strain