Materials and Design 109 (2016) 556–569

Contents lists available at ScienceDirect

Materials and Design

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

Mechanical properties and corrosion behavior of powder metallurgy iron-hydroxyapatite composites for biodegradable implant applications

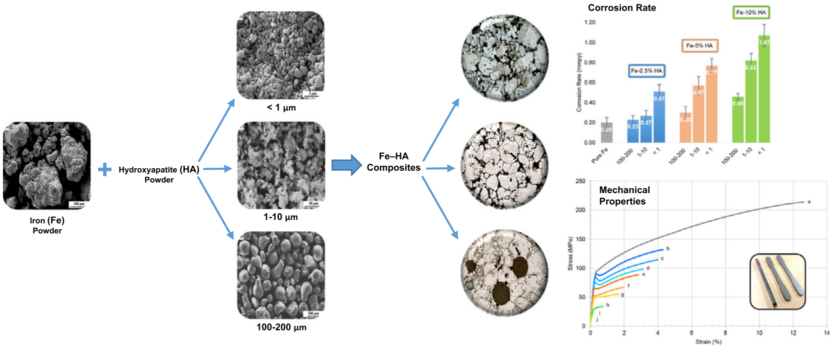
Mahdi Dehestani [a],*, Erik Adolfsson [b], Lia A. Stanciu [a]

[a] *Purdue University, Department of Materials Engineering, West Lafayette, IN 47907, USA*
[b] *Swerea IVF AB, Ceramic Materials, 431 53 Mölndal, Sweden*

HIGHLIGHTS

- Hydroxyapatite (HA) powders in three particle size groups (< 1 μm, 1–10 μm, 100–200 μm) were synthesized.
- Nine iron-hydroxyapatite composites (HA content = 2.5, 5, 10 wt%) were fabricated via the powder metallurgy process.
- Tensile strength and ductility of the composites decreased with increasing HA content and decreasing HA particle size.
- *In vitro* corrosion rates of the composites increased with increasing HA content and decreasing HA particle size.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 April 2016
Received in revised form 16 July 2016
Accepted 18 July 2016
Available online 20 July 2016

Keywords:
Biodegradable metal
Iron–hydroxyapatite composite
Powder metallurgy
Particle size
Mechanical properties
In vitro degradation

ABSTRACT

Nine Fe–HA composites were fabricated via powder metallurgy method by varying the amount (2.5, 5, 10 wt%) and particle size (<1 μm, 1–10 μm, 100–200 μm) of hydroxyapatite (HA) as a bioactive phase in the iron (Fe) matrix. X-ray diffraction did not detect any phase changes in HA after the sintering process. Uniaxial tensile tests measured the strengths of the composites. Polarization and immersion tests estimated the corrosion rates (CR). Yield strength, tensile strength, and ductility of the composites decreased with increasing HA content and decreasing HA particle size, whereas their corrosion rates increased. The strongest composite was Fe–2.5 wt% HA (100–200 μm) with $\sigma_y = 81.7$ MPa, $\sigma_u = 130.1$ MPa, fracture strain of 4.87%, and CR = 0.23 mmpy. The weakest composite was Fe–10 wt% HA (<1 μm) which did not exhibit plastic deformation, fractured at $\sigma_u = 16.1$ MPa with 0.11% strain, and showed the highest CR of 1.07 mmpy. This study demonstrates how the relative particle size between Fe and HA determines the mechanical and corrosion properties of Fe–HA composites, thereby aiding in enhancing future resorbable implant designs. The model can also be used when designing other bioactive composites (i.e. Ti–HA, Mg–HA) via powder metallurgy.

---

* Corresponding author.
E-mail addresses: mdehesta@purdue.edu (M. Dehestani), erik.adolfsson@swerea.se (E. Adolfsson), lstanciu@purdue.edu (L.A. Stanciu).

http://dx.doi.org/10.1016/j.matdes.2016.07.092
0264-1275/

1. Introduction

The importance and usefulness of developing metallic biodegradable alloys from iron (Fe) and magnesium (Mg) for hard tissue repair and bone reconstruction in orthopedics have been highlighted extensively in the biomaterials community over the past decade [1–3]. The concept of biodegradable metals is "providing a temporary support on healing process of a diseased tissue and progressively degrade thereafter" [3]. There is no need to perform a secondary surgery for implant removal since biodegradable bone fixtures in forms of rods, plates, screws, and anchors are supposed to provide initial mechanical support and dissolve gradually into the physiological environment without inducing toxicity as the new bone tissues replace the implant during the healing process. A progressive drop in mechanical strength and integrity of the implant through degradation also facilitates a gradual load transfer from the implant to the bone, which minimizes the stress shielding effect [4].

Principal requirements in the design of biodegradable metals for orthopedics are not limited to their mechanical stability, degradation characteristics, and cytotoxicity. In order to establish bone ingrowth and promote a stable bond at the interface between bone and implant material, the implant surface needs to be bioactive to assist osteoconductivity through bone cells growth and nucleation of biological apatite [5,6]. Hydroxyapatite (HA) with stoichiometry of $Ca_{10}(PO_4)_6(OH)_2$ has been widely used in the biomaterials field as both a bioactive bone substitute and a coating material due to its excellent biocompatibility and chemical similarity to mineral phase of the human bone, which is mainly composed of calcium (Ca) and phosphorous (P) [7–12]. HA has been incorporated into titanium (Ti) matrix to develop tailored composites for orthopedic and dental applications [13–21]. HA has also been added to Fe [22] and Mg [23–28] metals to improve the bioactivity of these matrices for biodegradable implant applications.

Pure Fe has been proposed for biodegradable cardiovascular stents [29] and hard tissue scaffolds [30,31]. Regardless of their slow degradation rates, iron alloys are attractive options due to their favorable mechanical properties for load-bearing applications [1–3]. Combining the inherent strength and ductility of pure iron matrix with markedly bioactive phases like HA and tricalcium phosphates (TCP) is an appealing approach for the design of composite materials for biodegradable bone fixation devices and scaffold applications. Past researchers have prepared such Fe–bioceramic composites via powder metallurgy route [22,32]. When compared with pure iron, the Fe–HA and Fe–TCP composites studied by Ulum et al. [22] exhibited increased in vitro degradation rates and a higher cellular activity was observed in their cytotoxicity test results. The implantation of these materials in sheep animal models monitored by X-ray radiography showed a consistent healing process of the tissue [22]. In another study [32], a Fe–40 vol% β-TCP composite prepared by powder injection molding showed a 28% higher corrosion rate than pure Fe after 56 days of immersion in 0.9% NaCl solution. The material experienced <1% decrease in compressive yield strength after the immersion period whereas the strength of pure iron dropped by 44%.

There is currently a fast growing trend in the use of biodegradable Mg-based materials due to their excellent biocompatibility, high specific strength, safe degradation, and mechanical properties which are close to those of human natural bone [33]. Several studies have adopted the conventional powder metallurgy method to prepare Mg–HA composites [23–28]. Gu et al. [23] prepared Mg–HA composites (10, 20, 30 wt% HA) and demonstrated that yield strength, tensile strength and ductility of the composites decreased with increasing HA content whereas their corrosion rates increased. In a recent study [24], Khalajabadi et al. blended nanoparticles of HA and MgO with Mg matrix and investigated the microstructure, biocorrosion, biocompatibility and physical properties of the Mg/HA/MgO composite system when the amounts of constituents varied. Khalil et al. [27] utilized high-frequency induction heat sintering (HFIHS) and optimized the processing parameters to achieve high density nanostructured Mg-1 wt% HA composites and investigated their microstructural features and mechanical properties. Witte et al. used AZ91D magnesium alloy as matrix and fabricated an AZ91D-20 wt% HA composite [28]. They improved the mechanical properties of the composite by including a hot extrusion step after sintering. Also, HA agglomeration during processing and its impacts on mechanical and corrosion properties of the Mg matrix were discussed.

Despite recent advances in the field of biodegradable metal, no effort has been made to date to gain an understanding of the mechanical properties of Fe–bioceramic composites and the reported strength data have been limited to compressive strength measurements [22,32]. Moreover, a critical characteristic of raw powders like particle size and its impact on final sintered microstructure, strength, and degradation rates of materials have not been studied. In general, the majority of the works published on enhancing the bioactivity of metallic biomaterials by incorporation of HA particles have overlooked the particle size effect. Therefore, this paper aims to present a systematic study that investigates the tensile strength variation of powder metallurgy derived iron-hydroxyapatite (Fe–HA) composites based on their composition and HA particle size. Additionally, in vitro degradation behavior, microstructures and fractography of the test specimens are presented too.

2. Materials and methods

2.1. Powder processing

The iron powder used in this study was ABC100.30 (Höganäs AB, Sweden), a water-atomized powder (0.002 wt% carbon and 0.04 wt% oxygen) with approximate particle size in the range of 30–200 μm. Three batches of hydroxyapatite powder having identical chemistry but different particle size distribution below 1 μm (<1 μm), 1–10 μm, and 100–200 μm were prepared. All different particle sizes used were prepared from the same powder of hydroxyapatite (Plasma Biotal, UK). A water-based suspension with high solid loading of the hydroxyapatite powder was prepared. The suspension was sprayed into liquid nitrogen followed by freeze drying to transform the frozen droplets to granules. From these, granules with a size of 125–250 μm were collected by sieving. When the collected granules were sintered at 1250 °C for 2 h, the sintering shrinkage reduced the granule size to around 100–200 μm. The remaining material with other sizes were also sintered at 1250 °C for 2 h and used to prepare the finer particle fractions.

When various particle sizes below 30 μm are to be selected, sieving is no longer a suitable method. The finer particles were thus obtained by sedimentation in water. The sedimentation procedure was repeated several times to divide the powder into different fractions with a narrow particle size distribution. To finally remove the water from the particles in the sediment without agglomerates to be formed, the sediment was frozen and freeze dried. From these fractions, one with a particle size of around 10 μm was selected. The finest powder with a particle size below 1 μm was finally prepared by ball milling with zirconia milling media. The milled suspension was frozen in liquid nitrogen without any additives and freeze dried to avoid agglomeration of the fine powder particles. Finally, all powder fractions prepared were reheated to 900 °C for 2 h in air to ensure that the particles surfaces had the same chemical and thermal history, since the particles surfaces may vary depending on how the final surface of the particle was formed which could be as sintered, a fractured surface caused by milling or in contact with water for an extended time during the preparation process.

2.2. Sample fabrication

Standard tensile test specimens for powder metallurgy materials were fabricated in this work according to the E8/E8M — 13a standard [34]. To design and make the relevant powder compaction die, ISO 2740 standard [35] was used. The iron (Fe) and hydroxyapatite (HA)