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Microstructural and mechanical properties of biodegradable iron foam prepared by powder metallurgy

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ABSTRACT

Research into biodegradable porous materials has been increasingly focused on iron-based materials because such materials possess suitable properties for orthopedic applications. In this study, we prepared porous iron with porosities of 32–82 vol.% by powder metallurgy using ammonium bicarbonate as a space-holder material. We studied the influence of initial powder size and compacting pressure on sample microstructure, contamination and mechanical characteristics. The experimental results were analyzed as well, using Gibson–Ashby model and this analysis showed a good agreement in theoretical and experimental data. Whereas increasing compression pressure decreased porosity, the use of finer iron powder led to an increase in porosity. Increasing the amount of space-holder material in the initial mixture increased the total porosity, improved compressibility and consequently decreased the number of pores originating from imperfect compaction. A higher compacting pressure and the use of finer powder enhanced both the flexural and compressive properties. Even the most porous samples prepared from the fine iron powder possessed mechanical properties comparable to human cancellous bone. Based on these results, we can claim that the use of fine initial iron powder is necessary to obtain highly porous iron, which appears to be suitable for orthopedic applications.

1. Introduction

The number of orthopedic reconstruction procedures has been increasing because of traumas, tumors, deformations, degeneration and diseases caused by an aging population [1]. The implants can be made of metallic, ceramic, polymer or composite material [1–3]. Metals and composites with metallic matrices possess high ductility and mechanical strength; therefore, they appear to be the most suitable materials for load-bearing orthopedic applications [4]. The orthopedic implants can be either permanent or temporary [5–7]. Metallic implants are usually made of stainless steel, titanium, titanium alloys or cobalt-based alloys [5,6] and are used for applications such as permanent joint replacements [5]. Temporary implants such as nails and screws that are made of such inert materials are usually removed after the injured tissue heals, but a second surgical intervention poses added risk. Therefore, biodegradable materials have been extensively investigated in recent decades [4,6,8–14].

There are known biodegradable materials based on ceramics, glass and polymers; however, their mechanical properties are not suitable for orthopedic purposes, in contrast to those of metals [1,2,15–20]. Three metallic systems, based on magnesium, zinc and iron, have been predicted as possible materials for the fabrication of biodegradable load-bearing orthopedic implants [7,9–14, 17,19,21–26]. A majority of the available investigations have been performed using magnesium-based materials because magnesium is a non-toxic element and its mechanical behavior is relatively similar to human bone. The limitations of magnesium-based materials are their high degradation rate and the fact that magnesium corrosion is linked to hydrogen evolution. The excess evolution of hydrogen often leads to the formation of hydrogen bubbles and drastically complicates the healing process. Therefore, magnesium-based materials seem to be suitable for the fabrication of small implants that have a lifespan of approximately 6–12 months [6,14,24,27]. Zinc shows similar mechanical properties to magnesium; however, its corrosion resistance in body fluids is significantly enhanced in comparison with magnesium [12]. Iron possesses significantly higher values of mechanical properties than do the previous mentioned materials. Iron is also a plentiful element in the human body and is necessary for the good functionality of many enzymes and oxygen transportation. Its corrosion in

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body fluids is not connected with hydrogen evolution, and its corrosion rate is significantly lower than that of magnesium. The *in vitro* tests of cytotoxicity and *in vivo* tests of biocompatibility have been performed in several studies [11,13,22,23,28] and all of them have shown that iron based materials are suitable materials for biodegradable load-bearing implants.

The corrosion rate of iron in the body is so slow that it must be enhanced for use in implantology. The other disadvantage of iron is its ferromagnetic behavior, which is undesirable for medical applications because it will cause problems during magnetic resonance imaging [6,9–11,18,21–23,28].

Fortunately, the ferromagnetic behavior of iron can be eliminated by alloying approximately 30 wt.% of manganese, which transforms the ferritic structure to an austenitic one. Moreover, alloying iron with manganese enhances the corrosion rate, which is also desirable for biodegradable implants. Alloying with noble metals, such as silver, platinum or palladium, or with elements, such as carbon and phosphorus, was found to be another way to enhance the corrosion rate [4,6,9–11,13,14,21–23,28]. The other problem with the use of iron-based materials is their high elastic modulus compared with human bone. The high elastic modulus might lead to the stress-shielding effect and, as a consequence, suppress bone regeneration. The elastic modulus can be made closer to that of human bone by increasing the porosity; moreover, the open-cellular porous structure is typical for cancellous bone and is thus desirable for many orthopedic implants. This type of implant is often called scaffold or bone augmentation. The open-cellular structure of such implants not only has mechanical behavior closer to bone, but it also allows for the transport of body fluids through the implant and the ingrowth of new tissue in the implant; further, it can serve as a drug carrier. Implants with such a structure also have relatively large surface areas, which causes a significantly higher degradation rate compared with non-porous materials [2–4,29–35].

The fabrication of porous metallic materials is possible through rapid prototyping, casting, foaming, powder metallurgy and many other methods [1,7,36–38]. Rapid prototyping is one of the most precise methods and allows for the fabrication of products that have very complicated shapes and structure. However, these methods are very expensive, which limits their use to special applications [38]. Casting and foaming iron-based materials is very difficult due to the high density, high melting point, high surface tension and low viscosity of iron melt. The absence of an oxide layer on the metal-pore interface also complicates iron foaming. The GASAR process is useable for iron [39]; however, other casting and foaming methods that are used for aluminum and other metallic materials are usable, though with large limitations [40]. Therefore, new foaming processes have been suggested for iron-based materials. One was introduced in 2007 by Murakami and consists of foaming by CO and CO_2, which are formed by reactions between carbon and Fe_2O_3 in a heated $Fe–Fe_2O_3–C$ mixture [41]. Another process was published in 2014 by Murakami and consists of foaming of a $FeO–Fe_2O_3–CaO–Al_2O_3$ slug and a subsequent reduction of the obtained porous oxide [40]. The disadvantages of these methods are inhomogeneity in the pore size and distribution; moreover, the products of the second method are contaminated by oxygen, aluminum and calcium [40,41]. Powder metallurgy seems to be the most suitable approach for making porous metallic biomaterials because it allows the fabrication of nearly final-shaped products with an interconnected porous structure possessing the desired properties. Though powder metallurgical techniques are usually more expensive than melting methods, they are significantly cheaper than 3D-printing or laser sintering. Typical representatives of powder metallurgy used for the fabrication of porous iron are the impregnation of a polyurethane foam and a space-holder technique [23,31]. The impregnation of a polyurethane foam method was successfully used to prepare iron-based foams in the past, and the samples showed an open-cellular structure. However, contamination, which is a serious issue for biomaterials, was not investigated in that study [23], though it can be expected according to the results obtained by Font et al. [42]. The space-holder method was performed to prepare biocompatible titanium, magnesium and iron. Urea and ammonium bicarbonate were usually used as space-holder materials [3,29–31,35,43,44]. In our opinion, ammonium bicarbonate is more suitable because it decomposes at significantly lower temperatures, which should eliminate any undesirable contamination.

Though many studies have been performed on porous metals prepared using a space-holder technique, to the best of our knowledge, only we have successfully used this method to prepare porous iron. In this paper, we focus on the influence of basic preparation parameters (compacting pressure and initial powder size) on the microstructural and mechanical properties of porous iron prepared using the powder metallurgy technique with ammonium bicarbonate as a space holder.

2. Materials and methods

Two types of iron powder, Strem Chemicals, 99.9 wt.%, 2–80 μm (maximal frequency approximately 20–30 μm) and Strem Chemicals, 99 wt.%, 10–200 μm (maximal frequency approximately 100 μm), and ammonium bicarbonate powder (Penta, p.a., 250–500 μm) were used as initial materials. The iron powders are named 'fine' (2–80 μm) and 'coarse' (10–200 μm) in this paper. Their morphologies are shown in Fig. 1, and the particle size distribution of the iron powders measured using an Analysette 22 NanoTec laser diffractometer is shown in Fig. 2.

The powders were manually blended into mixtures with an iron:ammonium bicarbonate volume ratio of 100:0, 80:20, 50:50 or 20:80. Hexane was added into the mixture during blending to make a dough-like mixture for enhanced homogenization and to avoid segregation. Blending was performed very carefully and gently in order to avoid breaking spacer particles. The mixtures were subsequently uniaxially cold-pressed into cylindrical green compacts (diameter 10 mm, length 40 mm) at room temperature. The compaction pressure was 510 MPa for the samples prepared from the coarse powder (0 and 20 vol.% of the spacer in the mixture) and 1020 MPa for the samples prepared from the fine powder (20, 50 and 80 vol.% of the spacer in the mixture) because the compaction pressure of 510 MPa was insufficient to compact the mixtures prepared from the fine powder. In addition, one series of samples prepared from a mixture containing the coarse iron powder and 20 vol.% of spacer was prepared using a compaction pressure of 1020 MPa to investigate the influence of compacting pressure on the studied characteristics. The sample designations used in this paper and conditions of their preparation are summarized in Table 1.

After the preparation, the green compacts were subjected to a two-step heat procedure. First, they were annealed at 130 °C for 4 h in air to decompose spacer particles. Second, they were sintered at 1000 °C for 4 h in an evacuated tubular furnace. Nine samples of each series were prepared. The sintered samples were weighed and measured to determine their porosities according to Eq. (1), where P is the sample porosity, d is the diameter, l is the length, m is the weight, and ρ is the density of pure iron (7.87 g/cm^3).

$$P = \left(1 - \frac{4 \cdot m}{l \cdot d^2 \cdot \pi \cdot \rho}\right) \cdot 100\% \qquad (1)$$