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Microstructural and mechanical characteristics of porous iron prepared by powder metallurgy

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ABSTRACT

The demand for porous biodegradable load-bearing implants has been increasing recently. Based on investigations of biodegradable stents, porous iron may be a suitable material for such applications. In this study, we prepared porous iron samples with porosities of 34–51 vol.% by powder metallurgy using ammonium bicarbonate as a space-holder material. We studied sample microstructure (SEM-EDX and XRD), flexural and compressive behaviors (universal loading machine) and hardness HV5 (hardness tester) of the prepared samples. Sample porosity increased with the amount of spacer in the initial mixtures. Only the pore surfaces had insignificant oxidation and no other contamination was observed. Increasing porosity decreased the mechanical properties of the samples; although, the properties were still comparable with human bone and higher than those of porous non-metallic biomaterials and porous magnesium prepared in a similar way. Based on these results, powder metallurgy appears to be a suitable method for the preparation of porous iron for orthopedic applications.

1. Introduction

In recent decades, research of biodegradable metallic materials has increased. Due to the mechanical properties of such materials, their application has focused on orthopedics and stents [1–8]. Many studies have been performed on magnesium-based alloys that have shown that these alloys are suitable for orthopedic purposes [8–13]. Unfortunately, these materials are only suitable for relatively small implants because their corrosion is connected to hydrogen evolution [14]; therefore, larger implants can be problematic because they release large amounts of hydrogen [3]. Additionally, their relatively short lifespan (approximately 12 months) can be unsuitable for some applications. Therefore, other metallic materials have been investigated as possible candidates for load-bearing applications in orthopedics [3].

Iron is a plentiful element in the human body and possesses higher mechanical properties than magnesium-based materials [3]. Therefore, iron has been studied as a possible material for biodegradable stents [1,2,15,16]. Although many in vitro studies of iron have shown that iron may be problematic [17,18], the in vivo studies performed by Peuster et al. [1,19] showed that implanted iron stents cause no significant toxicity issues. However, their degradation rate is too slow, and the stents cause problems similar to those of permanent stents [1,19]. Therefore, other authors have solved this problem by alloying iron-based materials to increase the degradation rate. Alloying with elements such as manganese, palladium, silver, phosphorus and silicon appears to be a suitable approach to increase the degradation rate and maintain sufficient mechanical properties and biocompatibility [2–5,15,16,20]. Another method to increase the degradation rate is the preparation of metal foams with an interconnected porous structure [19,21,22]. In addition to faster degradation, such materials allow the transport of bodily fluids to healing tissue and the ingrowth of new tissue into the implant; moreover, these materials possess lower Young moduli than do compact materials, which improves mechanical biocompatibility by preventing the stress-shielding effect [5,6,23–25]. These metal foams are very promising candidates for the preparation of bone replacements, also known as scaffolds. For example, Quadbeck et al. prepared a foamed iron alloyed by phosphorous and implanted it into a sheep's femur. Even after 12 months, no inflammation or toxicity was observed [5].

Generally, many methods exist for the fabrication of porous metallic materials [5,26–30], some of which were developed especially for iron [31]; however, not all of these methods are suitable for the fabrication of materials used in implantology. In addition to suitable mechanical and corrosion behaviors, such materials are not allowed to contain any harmful contaminants originating from the fabrication process. Moreover, an interconnected porous structure and a desirable pore-size interval are usually required for such materials. Casting to invert removable salt forms is problematic because of the high melting point of iron [6]. Therefore, powder metallurgical techniques seem to be more suitable for the preparation of porous iron implants because they allow the preparation of porous materials that possess the desired properties. Quadbeck et al. prepared iron-based foams by the impregnation of polyurethane foam with an iron-based slurry. Subsequently, the polyurethane foam was decomposed, and the porous body was sintered [5]. Unfortunately, many toxic compounds are generated during

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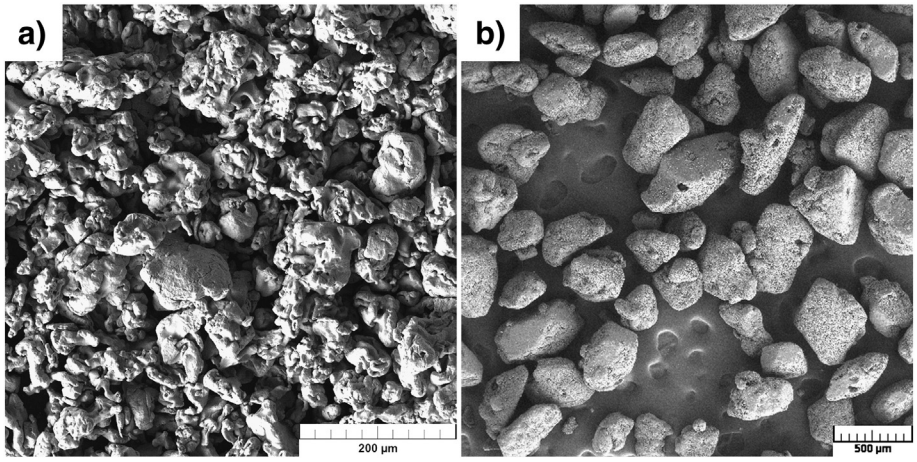

Fig. 1. Morphologies of the initial powders (SEM): a) iron and b) ammonium bicarbonate.

polyurethane decomposition, which may complicate the process [32]. Another powder metallurgical approach for the preparation of porous objects is a technique using space-holder particles. This approach, which has been successfully used for the preparation of porous magnesium and titanium [21,22,24,29], involves preparing a mixture containing particles of metal and some space-holder (such as urea or ammonium bicarbonate). The mixture is compacted, and the spacer particles are removed by low-temperature annealing or leaching. Subsequently, the porous body is sintered at higher temperatures [21,22,24,29].

Although many studies have been performed on the preparation of porous iron and its properties, to the best of our knowledge, none of these studies have addressed porous iron prepared by powder metallurgy using space-holder particles. Therefore, we prepared porous iron samples with different porosities using ammonium bicarbonate as a space-holder and studied the influence of increasing spacer content on the microstructural and mechanical characteristics of the materials.

2. Materials and methods

Iron (Alfa Aesar, 99.5 wt.%, <212 µm) and ammonium bicarbonate (Penta, p.a., 250–500 µm) powders were used as initial materials. Their morphologies are shown in Fig. 1, and the microstructure of the iron powder is shown in Fig. 2.

The powders were manually blended into mixtures containing 0, 5, 10, 15 and 20 vol.% of ammonium bicarbonate, which was used as the space-holder. Hexane was added into the mixtures during blending to make a dough-like mixture for better homogenization and to avoid segregation. These mixtures were uniaxially cold-pressed into cylindrical green compacts (diameter 10 mm, length 40 mm) using a compaction pressure of 510 MPa at room temperature. The compacts were annealed at 130 °C for 4 h in air to thermally decompose the ammonium bicarbonate particles. Subsequently, the porous bodies were sintered in an evacuated tubular furnace at 1000 °C for 4 h. The prepared 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).

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

Portions of the samples were cut both across and longitudinally, and metallographic sections were prepared in the standard way to observe sample microstructure using an Olympus PME3 light metallographic microscope (LM) and a TESCAN VEGA-3 LMU scanning electron microscope (SEM). The cross-sections were also subjected to EDX and XRD investigations to determine the level of contamination during sample preparation. EDX analyses were performed using an SEM equipped with an Oxford Instruments INCA 350 EDX analyzer (SEM-EDX). XRD analyses were performed using a PANalytical X'Pert PRO X-ray diffractometer equipped with a Cu anode. Five samples of each series were subjected to three-point bending tests, and three other samples with a

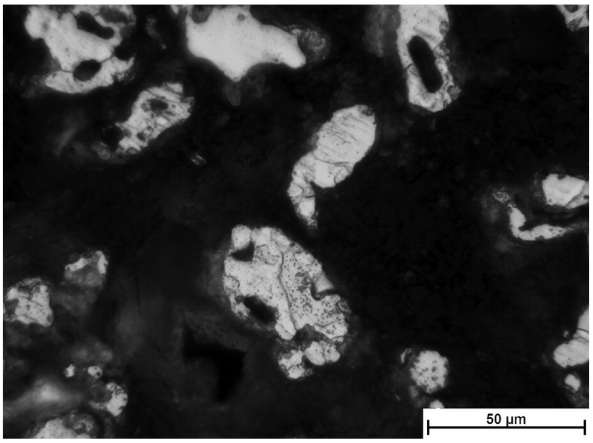

Fig. 2. Microstructure of iron powder (LM).

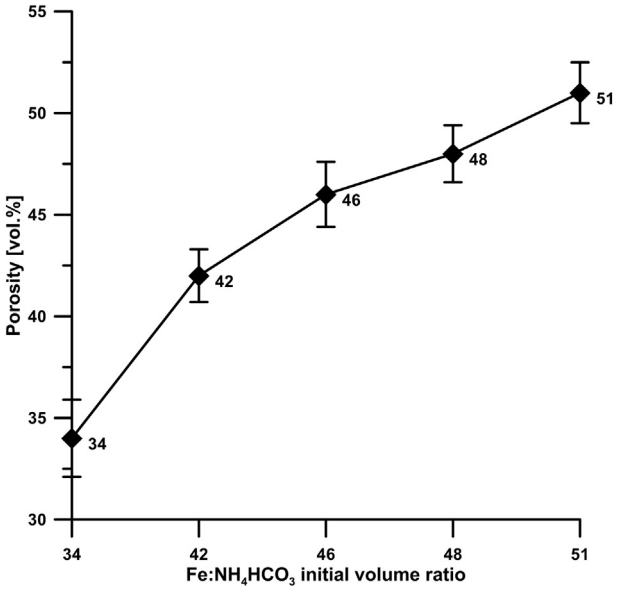

Fig. 3. Porosity versus initial Fe:NH_4HCO_3 volume ratio.