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Production and fluoride treatment of Mg−Ca−Zn−Co alloy foam for tissue engineering applications

Ilven MUTLU

Metallurgical and Materials Engineering Department, Istanbul University, Istanbul 34320, Turkey

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Abstract: Highly porous Mg−Ca−Zn−Co alloy scaffolds for tissue engineering applications were produced by powder metallurgy based space holder−water leaching method. Mg−Ca−Zn−Co alloy foam can be used as a scaffold material in tissue engineering. Carbamide was used as a space holder material. Fluoride conversion coating was synthesized on the alloy by immersion treatment in hydrofluoric acid (HF). Increasing Zn content of the alloy increased the elastic modulus. Ca addition prevented the oxidation of the specimens during sintering. Electrochemical corrosion behaviour of the specimens was examined in simulated body fluid. Corrosion rate decreased with Zn addition from 1.0% up to 3.0% (mass fraction) and then increased. Mass loss of the specimens initially decreased with Zn addition up to about 3% and then increased. Fluoride conversion coating increased the corrosion resistance of the specimens.

Key words: Mg−Ca−Zn−Co alloy; scaffold; fluoride treatment; metal foam; corrosion

1 Introduction

Scaffold provides support for cells, and its architecture determines the shape of new tissue. In general, bone substitute material should be osteoconductive, biodegradable and strong enough [1,2]. Several scaffold materials, including hydroxyapatite and polymers, have been investigated for tissue engineering. Brittle nature of ceramics and low strength of polymers have limited applicability of these materials. Stainless steels, Co alloys and Ti alloys have been studied in orthopaedic implants. However, they cannot degrade and a surgical operation is needed after tissues have healed [1,2].

Porous Mg has potential to use as a biodegradable scaffold for bone substitute applications [1,2]. Mg exhibits low corrosion resistance in physiologic environments [3−5]. Non-toxic oxides or hydroxides which formed during the degradation enhance activity of osteoblast and decrease amount of osteoclast during regeneration. These properties have attracted attention to the development of biodegradable Mg implants [1−3]. Mg alloys have closer elastic modulus to the bone compared with Ti alloys, better ductility and toughness than hydroxyapatite and higher strength than polymers. Another performance for degradable biomaterial is the degradation rate. It influences not only the healing period but also the loss of mechanical properties during degradation [2].

Studies on the Mg alloys are focused on corrosion and biocompatibility. Most Mg alloys contain Al and rare earth (RE) elements, whereas Al is neurotoxicant, and hepatotoxicity is detected after administration of rare earth. The main issue to limit application of Mg is its low strength and poor corrosion resistance. Commercial Mg alloys are well researched. Some Mg alloys, such as AZ31, AM60B and WE43 are attempted as biomaterials. Al, Mn, Zr and RE elements are employed to improve the mechanical and corrosion properties. However, these products result in negative effects on the human [3−6].

Zn is a grain refiner and enhances strength of the Mg. Mg−Zn alloys reveal the improved corrosion properties, which is attributed to the ability of Zn to form precipitates. Low volume fractions of MgZn decrease the corrosion rate, whereas larger volume fractions promote microgalvanic corrosion. Zn contents up to 5.6% (mass fraction) improve the corrosion properties. Since the maximum solubility of Zn in Mg is 8.4%, a high amount of Zn can be retained in the solid solution [3−5]. New

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Corresponding author: Ilven MUTLU; Tel: +90-5365718461; E-mail: imutlu@istanbul.edu.tr
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Mg−Zn alloy exhibits moderate mechanical properties and cytocompatibility. Mg−Zn alloys offer constant degradation rate owing to homogeneous microstructure. Zn improves corrosion resistance and mechanical properties of the Mg. Mg−Zn alloys possess the highest capacity for aging [1−6].

Ca refines the microstructure of the Mg alloys, and enhances the strength and corrosion resistance. Formation of a calcium−phosphate layer is observed during immersion in simulated body fluid, which points to a beneficial influence on cell adhesion and corrosion protection. In the Mg−Ca system, up to 0.5%−0.7% Ca produces superior mechanical and corrosion properties [3−5]. Wrought Mg alloys have low strength and low workability. Powder metallurgy overcomes these problems. Powder metallurgy is known to strengthen the material by its microstructure. Powder metallurgy is suitable for manufacturing Mg foam because of its high activity. In addition, space holder method is suitable for manufacturing open cell foams [7,8]. Mg−Zn alloy is a precipitation hardenable system, in which solubility of Zn decreases with the increase of temperature. Atomic radius of Zn is smaller than that of Mg. Another feature is that mixing enthalpy between solute elements is negative. During aging, decomposition of super-saturated solid solution results in formation of precipitates [9,10].

The addition of Co to the Mg−Zn alloy raises the eutectic temperature and induces response to aging. The microstructure of Mg−Zn−Co is finer than that of Mg−Zn. Intermetallics are refined by Co addition. Co permits use of higher temperature for solution, which leads to larger supersaturation of Zn atoms and higher concentration of vacancies in Mg grains after quenching. The increase in eutectic temperature permits use of higher solution temperature, ensuring supersaturation of Zn, which leads to larger fraction of precipitates [9−11]. Kinetics of aging is accelerated in Co-containing alloy. Co segregates into the intermetallics [9−11].

Mg alloys suffer from a high corrosion rate in body fluids. To improve the corrosion resistance, one of the ways might be coatings. There are several surface treatments for improving the corrosion resistance, but they are mainly developed for Mg alloys in industrial applications. The surface treatment methods include conversion coatings, carbonate treatment, alkali-heat-treatment, anodizing, polymeric coatings and electro-deposition. Surface treatment of Mg can be classified into conversion and deposition coatings. Conversion treatment via hydrofluoric acid is promising due to its simplicity and low cost. Mg alloys are resistant to hydrofluoric acid (HF) due to the formation of a protective layer of MgF_2. Corrosion resistance of Mg could be improved by fluoride treatment, since the fluoride ion is a corrosion inhibitor for Mg. By this method, corrosion rate decreases by providing MgF_2 protective layer. Moreover, one of the components of bone and teeth is fluorine. Fluoride coating has good bonding strength and can be performed on complex shaped parts [12−18].

SEYEDRAOUFIN and MIRDAMADI [1] prepared Mg−Zn scaffolds. According to their results, Mg−Zn alloy could be considered as scaffold materials. Porous Mg has potential to serve as a degradable scaffold for bone substitution. The dissolved Mg ions may promote bone cell attachment and tissue growth. BOBE et al [19] fabricated a biodegradable, open-porous, mechanically adaptable scaffold from Mg alloy by sintering. The in vitro environment influenced the corrosion rates compared with the in vivo environment. Culture media composition influences the ionic composition of the extract by selectively dissolving ions. AGHION et al [20] produced Mg foams by space holder method as a scaffold for drug delivery. The amount and delivery time of the released drug were controlled by space holder. WEN et al [21] produced Mg foams for scaffold applications. They investigated the mechanical properties of Mg with the porosity of 35%−55% and the pore size of 70−400 μm. Results indicate that the elastic modulus increases with decreasing porosity. The mechanical properties were close to those of human bone.

The purpose of this work is to study the novel Mg−Ca−Zn−Co alloy, with greater aging response. There has been no study on open-cell porous Mg−Ca−Zn−Co scaffolds produced by powder metallurgy. In this study, Mg−Ca−Zn−Co alloy foams were produced by powder metallurgy based on space holder method. Fluoride treatment was carried out by immersion treatment in HF. Although cast Mg−Ca−Zn/Mg−Ca−Zn−Co alloys were studied [3−5], studies on Mg−Ca−Zn−Co foams produced by powder metallurgy were limited. Since the corrosion rates in the literature are not as low as those required for implant applications, further investigations regarding an improved alloy composition design are required. In the range of the low alloyed Mg systems, the effect of alloying elements on the degradation behaviour has not been fully investigated.

2 Experimental

2.1 Foam production

Foams were produced by powder metallurgy based on space holder-water leaching method using Mg, Ca, Zn and Co powders (Alfa Aesar, USA). The purity of the powders was >99.5%. The mean particle size of the powders was about 34 μm. In the alloy preparation stage, 0.7% Ca, 1% Zn, 3% Zn, 5% Zn, 8% Zn and 0.3% Co, 0.6% Co powders were added to the Mg powder. The