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Synthesis and characterization of Ti−Co alloy foam for biomedical applications

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Abstract: Highly porous Ti−Co alloy specimens for biomedical applications were synthesized by powder metallurgy based space holder technique. Ti alloys have high melting temperature and affinity for oxygen, which makes Ti alloys difficult to be processed. The Co addition reduces the melting temperature and Ti−Co alloy was sintered at lower temperatures. The electrochemical corrosion behaviour of the specimens was examined in the artificial saliva solution. The effects of Co content of the alloy, the pH value and fluoride concentration of the artificial saliva solution on the electrochemical corrosion properties of the specimens were investigated. The microstructure and mechanical properties of the specimens were examined. The electrochemical impedance spectroscopy results indicate that the corrosion resistance of the specimens decreases at high fluoride concentrations and low pH value. The defect density increases with increasing the fluoride concentration and decreasing the pH value of artificial saliva according to Mott−Schottky analysis.

Key words: Ti−Co alloy; metal foam; powder metallurgy; electrochemical corrosion; biomedical implant

1 Introduction

Metal foams are used as energy absorbers, heat exchangers, filters and biomedical implants. Highly porous metal foams exhibit a structure similar to cancellous bone. The advantage of metal foams for implant applications is their ability to provide anchorage for the surrounding bone tissue via the ingrowth of tissue into the pores [1−5]. Biomedical implants suffer from mismatch of elastic modulus with surrounding bone. By adjusting the porosity content, the stiffness of implant can be controlled in order to reduce the stress-shielding effect between the implant and surrounding bony tissue due to the mismatch of the elastic modulus [1−5].

Ti alloys are used as biomedical implant because of their high specific strength, high biocompatibility and electrochemical corrosion resistance. However, there are disadvantages such as high elastic modulus, low wear resistance, high melting temperature and high affinity for oxygen [3−7]. High melting ranges and affinity for oxygen make the Ti alloys difficult to be processed. Ti alloy with Co addition has lower melting temperature, especially at eutectic composition. Co addition enhances the sinterability of Ti particles, and the compacts were sintered at lower temperatures than the traditional Ti alloys [7].

The applications of Co include wear, corrosion, and heat resistant Co-based alloys, Ni-based superalloys, Fe-based superalloys, cemented carbides and magnetic materials. Some Co alloys are biocompatible, which are used as biomedical implant. CoCrMo alloy is widely used in total hip and knee replacements and dental devices. They are preferred for particular applications with metal-on-metal contact for tribological properties [8−10]. The biocompatibility of Co alloys is based on the formation of a passive oxide film. Co is protected from the oxidation by this passive film [10]. The heating of Co in the oxygen produces Co_3O_4 which transforms to CoO at 900 °C. CoO is oxidized with water and oxygen to $Co(OH)_3$. The corrosion behaviour of Co in aqueous solutions depends on the composition and pH value. In neutral and alkaline solutions, the surface oxide film is stable. In the presence of chloride in the solution, pitting corrosion takes place [9].

In this study, highly porous Ti−Co alloy foams were produced for biomedical implant (hard tissue) applications. The Co addition reduced the sintering temperature of the Ti alloy. Ti−Co alloys were prepared with different Co contents in order to determine the

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optimum Co addition. Although there are some studies on the Ti−Co alloys, there is no study on the electrochemical corrosion properties of Ti−Co alloy and no study on highly porous Ti−Co alloy foams. The electrochemical corrosion studies on the metal foams are also scarce. The electrochemical corrosion behaviour of the specimens was examined by DC corrosion tests, electrochemical impedance spectroscopy (EIS) tests and Mott-Schottky analysis in the artificial saliva environment. The effects of Co content of alloy, pH value and fluoride concentration of the artificial saliva solution on the electrochemical corrosion behaviour of the specimens were evaluated. The microstructure and mechanical properties of the specimens were also examined.

2 Experimental

2.1 Foam production

Foams were produced by powder metallurgy based space holder−water leaching method using Ti and Co powders (Alfa Aesar, USA). The chemical composition of Ti powder was 99.61% Ti, 0.23% O, 0.018% N, 0.03% Fe, 0.01% Mn, 0.01% Mg, 0.009% C, <0.01% Al, 0.01% Cl, <0.01% Na and 237×10^{-6} H (mass fraction). The chemical composition of Co powder was 99.7% Co and 0.15% O (mass fraction). The mean particle size of the irregular shaped Ti and Co powders were 44 and 34 μm, respectively. In the alloy preparation stage, 3%, 5%, 7% and 10% Co (mass fraction) powder were added to the Ti powder. As a space holder, carbamide (Merck, Germany) in the fraction of 710−1000 μm was used. The binder for green strength was polyvinylalcohol (PVA). The metal powders were mixed with 1.5% PVA (mass fraction). The mixtures were compacted at 200 MPa into cylindrical specimens with diameter of 12 mm. The specimens were immersed in water and then carbamide was leached out. The sintering cycle consisted of heating at a rate of 5 °C/min to 400 °C (debinding) with dwell time of 40 min, followed by heating at a rate of 11 °C/min to the sintering temperatures. The specimens were sintered at temperatures between 1000 and 1100 °C for 45 min. The sintering was performed in high purity argon gas atmosphere in a horizontal tube furnace (Lenton, UK). The dimensions of the cylindrical sintered specimens were about 11.9 mm in diameter and 16−18 mm in height.

2.2 Characterization of microstructure and mechanical properties

The microstructure of specimens was examined by a field emission gun-scanning electron microscope (FEG-SEM, FEI Quanta FEG 450). Energy dispersive spectroscopy (EDS) analysis was carried out to study the chemical composition of the surface. In the metallographic examinations, the sintered specimens were ground, polished and etched. The etchant was Kroll’s reagent, which was composed of 3 mL HF, 6 mL HNO_3 and 91 mL H_2O. The SEM images of the sintered specimens were used to determine the mean pore size, pore size distribution and pore shape of the foams using image analyzer software (Clemex Vision, PE). The density and total porosity content were determined from the measurements of mass and dimensions of the cylindrical specimens. The mechanical properties of the sintered specimens were studied by compression tests performed on a Schimadzu AG-X materials testing machine.

2.3 Artificial saliva preparation

Artificial saliva solution was prepared from chemicals supplied by Merck, Germany [4,11−14]. The compositions of reagents are 0.40 g/L NaCl, 0.79 g/L $CaCl_2\cdot H_2O$, 0.40 g/L KCl, 0.005 g/L $Na_2S\cdot 9H_2O$, 0.78 g/L $NaH_2PO_4\cdot H_2O$, 0.35 g/L carbamide. In oral environment, in which the pH value ranges from 2 to 11, the fluoride concentration has effect on the implants. There is increased use of gels containing fluoride to prevent plaque and caries [25−31]. In order to determine the effect of fluoride on the implant, artificial saliva solutions with 0.25%, 0.50%, 0.75% and 1.00% F^- were prepared using NaF addition. The pH value was adjusted to 2.50, 5.00 and 7.40 by adding lactic acid. The pH value of the artificial saliva solution was measured and monitored using a pH meter (WTW, inoLab 720, Germany). The metal ion release was investigated by static immersion tests. Inductively coupled plasma-mass spectrometer (ICP-MS) (Thermo Scientific Elemental X Series 2) was used to determine the metal (Ti and Co) ion release. 70% porous specimens were cut along longer axes and semi-cylindrical specimens were obtained. Then, the specimens were polished and washed. The porosity and surface area values of each specimen were equal in the immersion tests. The specimens were then exposed to artificial saliva solution (50 mL) in closed polyethylene bottles. The foams with equal porosity (70%) were immersed in the artificial saliva solution. The ratio of solution volume to specimen surface area was constant in all immersion tests. An artificial saliva solution without a specimen was used for blank test in ICP measurements. The area of the pores was subtracted from total surface area of the foams to find actual solid surface area.

2.4 Electrochemical corrosion study

Electrochemical corrosion studies were carried out in the artificial saliva solution using a potentiostat (Interface 1000 Potentiostat/Galvanostat/ZRA, Gamry