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Influence of Fluoride Content of Artificial Saliva on Metal Release from 17-4 PH Stainless Steel Foam for Dental Implant Applications

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Highly porous 17-4 PH stainless steel foam for implant applications was produced by space holder technique. Metal release and weight loss from 17-4 PH stainless steel foams were investigated in fluoride added artificial saliva environment by static immersion test. An inductively coupled plasma-mass spectrometer was employed to measure the concentrations of various metal ions. Effects of fluoride content of artificial saliva on metal release and weight loss from the steel foams were investigated. Effects of immersion time, pH value and process parameters on the weight loss and metal release were determined. Pore morphology, pore size and mechanical properties of the 17-4 PH stainless steel foams were also characterized.

KEY WORDS: Metal release; Dental implant; Metal foam; Fluoride; Artificial saliva

1. Introduction

Development of metallic implants for replacement of hard tissues is important in orthopedic applications. In dentistry, metals are used as implant in reconstructive surgery to replace a tooth, or in production of prostheses such as plates, crowns, bridges, braces and archwires. These materials are exposed to oral cavity, which is a corrosive environment. Corrosion of implants is critical because it can reduce the biocompatibility and mechanical properties. Release of metals can result in adverse effects including toxicity, carcinogenicity, and allergy[1–5]. Stainless steels, Ti alloys and Co alloys are widely used as load-bearing implants. Corrosion resistance of stainless steels depends on chemical composition, microstructure, surface condition, and production route[5–9].

Alloys that are used in dentistry are exposed to oral environment. Saliva acts as an electrolyte, which can cause corrosion. The pH of saliva is between 2 and 11 while temperature is between 0 and 70 °C[10–17]. Corrosion behavior and metal release of implants must be studied in saliva or artificial saliva. In the oral environment concentration of fluoride has an effect on corrosion of implants. There is an increased use of dental gels and rinses containing fluoride to prevent plaque and caries. Fluorides are harmful to metals, especially in low pH. Addition of fluoride to solution makes the metal more active and accelerates corrosion. Incorporation of fluoride in oxide layer reduces the protective properties. Low pH increases corrosion rate in the presence of fluoride, due to hydrofluoric acid formation. Dental bleaching and fluoride treatment agents are used for esthetic purposes and prevention of plaque. Corrosive effect of fluoride on dental materials has not been well studied[11–17].

Metal foams are used as energy absorbers, filters, heat exchangers, and biomedical implants. Space holder technique has been used to produce foams from steels and titanium which have relatively high melting temperatures. This process produces interconnected porous structure with high porosity suitable for implants. Foams exhibit a porous structure similar to cancellous bone. Use of metal foam as implant allows mechanical linking of bone with implant by bone tissue ingrowth into pores. Additionally, by adjusting the porosity, stiffness can be controlled to reduce stress-shielding effect between implant and bone. Requirements for implant materials are biocompatibility, open porosity, low density, corrosion resistance, wear resistance, mechanical strength close to cancellous bone and commercialization potential[18–27].

Dental implants can have three types of macro designs: screw thread design, solid body press-fit design and porous-coated design. While the threaded design is the most popular, porous-coated implants have also been used. They are used as abutments for over dentures, replacing missing teeth in narrow areas. Porous implants improve contact at implant–bone interface, provide areas for bone ingrowth and improve fixation to bone[28–30].

In the present study, immersion tests were carried out in fluoride added artificial saliva solution using 17-4 PH stainless steel foams. Traditional AISI 316L austenitic stainless steels are used in biomedical applications. However, these steels have high

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Ni, which lead to metal sensitivity, allergy and other complications when released. 17-4 PH stainless steel has lower Ni content. In addition, 17-4 PH stainless steel has higher mechanical properties and its mechanical properties can also be improved by aging. 17-4 PH stainless steel is used in aerospace, chemical, food processing and biomedical applications. 17-4 PH stainless steel has combination of strength, hardenability (aging), and corrosion resistance not found in any other steel grade. Advantages of steel foams are their ability to provide mechanical anchorage for surrounding tissue, low density and sufficient strength close to bone. In the present study, 17-4 PH stainless steel foams were immersed in fluoride added artificial saliva solutions and then metal release and weight loss were determined. The effect of fluoride content in artificial saliva on stainless steels has not been well documented. In this study, effects of fluoride concentration, pH and immersion time on metal release were investigated.

2. Experimental

2.1. Steel foam production

Starting material for the foam production was gas atomized 17-4 PH stainless steel powder (Carpenter, Sweden) with spherical morphology. The chemical composition of the steel powder was Fe − 4.6% Ni, 15.2% Cr, 0.7% Mo, 0.4% Nb, 4.9% Cu, 1.4% Si, 0.07% C. Mean particle size of the powder was 14.6 μm. As a space holder, carbamide (Merck, Germany), in fractions of 1000−1400, 710−1000, 500−710 μm with irregular shape and the fraction of 1000−1400 μm with spherical shape, was used for its high solubility in water. To enhance sintering, 0.5 wt% boron (Merck, Germany) was added to the steel powder to create a liquid phase during sintering. The binder for green strength was polyvinylalcohol (PVA), supplied by Merck, Germany. PVA was preferred for its biocompatibility. 2.5 wt% PVA was added to the steel powder. The mixture was compacted at 180 MPa into cylindrical specimens of 12 mm in diameter and 17 mm in height. Green specimens were immersed in water at room temperature and ∼90% of the carbamide was leached out in ∼10 h. Thermal debinding temperature of the PVA was determined to be ∼410 °C by using thermo gravimetric analysis (TA, SDT Q600). The PVA was thermally removed as part of sintering cycle, which consisted of heating at a ramp rate of 5 °C/min to 410 °C (debinding) with a dwell time of 40 min, followed by heating at a rate of 10 °C/min to sintering temperature. The foams were sintered at 1260 °C for 40 min in H_2. In addition, the foams were aged to further enhance the mechanical properties. At the aging stage, sintered foams were austenitized at 1050 °C in a vacuum furnace and then quenched using N_2 (0.6 MPa (6 bar)) as a cooling gas. Quenched specimens were then aged for 4 h at 480 °C in H_2.

2.2. Artificial saliva preparation

Artificial saliva solution was prepared from calculated amounts of chemicals supplied by Merck, Germany according to procedure described in literature[10−17]. The amount of chemical reagents for preparing artificial saliva solutions are given in Table 1. The chemical reagents were added to the solutions in the order they are listed.

In preparation of artificial saliva, firstly 750 ml of distilled water was put into a 1000 ml beaker. The temperature was kept at 37 °C.

Table 1 Amount of chemical reagents for preparation of artificial saliva

Reagent	Amount (g/l)
NaCl	0.40
$CaCl_2$ $2H_2O$	0.79
KCl	0.40
Na_2S $9H_2O$	0.005
NaH_2PO_4 H_2O	0.78
Urea−$CO(NH_2)_2$	1.00

Chemical reagents were added into the water one by one. The pH meter (WTW inoLab 720, Germany) was calibrated with standard buffer solutions. After addition of the chemicals, the temperature of the solution was checked, and the electrode (WTW SenTix 81, Germany) of the pH meter was placed in the solution. After the adjustment of pH, the solution was transferred from the beaker to a flask of 1000 ml. Distilled water was added to the solution, to adjust the total volume to 1000 ml. Artificial saliva with varied pH values were prepared to study the effect of the pH on metal release. In order to determine the effect of fluoride on implant, artificial saliva solutions with 0.25, 0.50, 0.75 and 1.00 wt% F concentrations were prepared using NaF addition. The pH was adjusted to 2.30, 3.20, 5.80 and 7.40. The pH was lowered by adding lactic acid. This acid was chosen since it is naturally released by bacteria. The pH of fluoridated odontological gels is ∼4.00, and after a meal, pH of buccal cavity can fall below this value.

2.3. Static immersion test

70% Porous specimens were cut along longer axes and semicylindrical specimens were obtained. Thus, maximum solid surface area, which was exposured to solution, was obtained. Then, the specimens were machined, polished and washed. Porosity and surface area of each specimen were equal in immersion tests. Specimens were then exposed to artificial saliva. Foams with equal porosity levels (70%) were immersed in artificial saliva at 37 °C for several soaking times up to 14 days. Solution volume to specimen surface area ratio was constant in all immersion tests. The inductively coupled plasma-mass spectrometer, ICP-MS (Thermo Scientific Elemental X Series 2) was employed to measure the concentrations of major metal ions like Fe, Cr, Ni, Cu and Mo. A solution without a specimen was used for blank test. After different soaking periods, the foams were removed from the solutions. Then the specimens were rinsed with water and dried. The dried specimens were weighed and weight loss was determined.

2.4. Characterization of microstructure and mechanical properties

The microstructures of the foams were observed by scanning electron microscopy (Jeol 5600), field emission gun-scanning electron microscopy (FEI Quanta 450, FEG-SEM) and optical microscopy (ME600 Nikon). Energy dispersive spectroscopy (EDS) analysis (IXRF systems 550i) was carried out to study chemical composition. The digital images of the foams were used to determine the mean pore size and shape by using an image analyser (Clemex Vision, PE). Total porosities were determined from measurements of weights and dimensions. Open porosity contents of the foams were measured by using a Hg porosimeter (Quantachrome Poremaster). Mechanical properties were studied by compression test (Zwick-Roell Z050).