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Characterization of 17-4 PH stainless steel foam for biomedical applications in simulated body fluid and artificial saliva environments

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ABSTRACT

Highly porous 17-4 PH stainless steel foam for biomedical applications was produced by space holder technique. Metal release and weight loss from 17–4 PH stainless steel foams was investigated in simulated body fluid and artificial saliva environments by static immersion tests. Inductively coupled plasma-mass spectrometer was employed to measure the concentrations of various metal ions released from the 17-4 PH stainless steel foams into simulated body fluids and artificial saliva. Effect of immersion time and pH value on metal release and weight loss in simulated body fluid and artificial saliva were determined. Pore morphology, pore size and mechanical properties of the 17-4 PH stainless steel foams were close to human cancellous bone.

1. Introduction

Metal foams offer opportunities for a wide range of applications, such as energy absorbers, heat exchangers and biomedical implants [1–4]. Space holder technique has been used to produce foams from stainless steels and titanium which have high melting temperatures. This process also produces open-cell structure with sufficient porosity suitable for biomedical applications [5–7]. Open-cell foams exhibit a porous structure similar to cancellous bone. Use of metal foam as implant allows mechanical anchorage of bone with implant by bone tissue ingrowth into the pores. Additionally, by adjusting the porosity, stiffness can be controlled in order to reduce the stress-shielding effect between implant and bone [5–8]. Requirements for implant materials are biocompatibility, open porosity, low density, corrosion resistance, wear resistance and sufficient mechanical strength close to bone [8–11].

Corrosion of biomaterials is critical because it can affect the biocompatibility and mechanical integrity. Release of metal ions can result in adverse reactions including toxicity, carcinogenicity and genotoxicity [12]. Stainless steels, Ti alloys and Co alloys are widely used as load-bearing implants. Implants fabricated from Co-based alloys produce elevated Co, Cr and Ni concentrations. Ti–6Al–4V alloy has been used as implant and the cytotoxicity of V is an issue of concern. V is considered to be an essential element, but may become toxic at high levels [13]. Cr toxicity is related to its valence state. Cr^{3+} is the actual agent of toxicity. Corrosion resistance of stainless steels is a function not only of chemical composition but also of microstructure, surface condition, and production route, all of which may change the thermodynamic activity of surface [14,15].

The environment of the human body is buffered so that the pH is maintained at ~7.40 at 36.5 °C. Different parts of body may have different pH and oxygen concentrations. Moreover, pH can change in tissue that has been infected. In a wound, pH can be ~3, and in an infected wound pH can increase to ~9 [16,17]. Two features control the severity of this environment. Firstly, the saline solution is an excellent electrolyte and facilitates corrosion. Secondly, there are molecules that catalyze certain reactions. Corrosion behavior of materials can be studied using simulated body fluids (SBF) which simulates the inorganic part of blood plasma. These tests are focused on the examination of materials and provide information to evaluate their suitability for biomedical applications [18–22]. A comparison of nominal concentrations of ions in human plasma and in simulated body fluid at pH of 7.4 is given in Table 1.

Metals that are used in dentistry are exposed to changeable conditions of oral environment. Saliva contains organic and inorganic substances suspended in an aqueous medium. The pH of saliva may vary between 2 and 11 while the temperature may be between 0 and 70 °C. Saliva is dependent on the age, eating habits, and oral hygiene [23–25]. Hence, corrosion behavior and metal release of materials for dental applications must be studied in artificial saliva.

In the present study, we characterized the 17-4 PH stainless steel foams for biomedical applications by immersion tests in simulated body fluid and artificial saliva. The 17-4 PH stainless steel is used for applications in the aerospace, chemical and food processing industries and in biomedical applications. Traditional AISI 316L and AISI 304 austenitic stainless steels are used in biomedical applications. However, these steels contain high amount of Ni to maintain their austenitic microstructure. Nickel may lead to metal sensitivity when released. 17-4 PH

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Table 1
Ion concentrations of a simulated body fluid (SBF) and human blood plasma [16,17].

Ion	Ion concentration, mM	
	Simulated body fluid	Human blood plasma
Na^+	142.0	142.0
Ca^{2+}	2.5	2.5
K^+	5.0	5.0
Mg^{2+}	1.5	1.5
Cl^-	147.8	103.0
HCO_3	4.2	27.0
HPO_4^{2-}	1.0	1.0
SO_4^{2-}	0.5	0.5

stainless steel has relatively lower Ni content than these austenitic stainless steels. In addition, 17-4 PH stainless steel has higher mechanical properties and its mechanical properties can also be improved by aging. In metal foams, mechanical properties are connected to density. In the foams, density cannot always be varied and in order to control mechanical properties, heat treatment is desirable. 17-4 PH stainless steels offer a combination of strength, ease of heat treatment (aging), and corrosion resistance not found in any other steel grade. The advantages of steel foams are their ability to provide mechanical anchorage for the surrounding tissue via ingrowth of tissue into pores, low density and sufficient strength close to bone. For implants, the effect of implant on body and effect of body on implant are major considerations before implant is approved for use. In the present study, 17–4 PH stainless steel foams were immersed in simulated body fluids and artificial saliva. Metal release and weight loss was determined. Effects of pH and immersion time on metal release were investigated.

2. Experimental

Starting material for foam production was 17–4 PH stainless steel powder (Carpenter, Sweden) with spherical morphology. The chemical composition of the powder was Fe, 4.6 wt.%; Ni, 15.2 wt.%; Cr, 0.7 wt.%; Mo, 0.4 wt.%; Nb, 4.9 wt.% Cu, 1.4 wt.%; Si, 0.07 wt.% C. Mean particle size of the steel powder was 14.6 μm. As a space holder, carbamide (Merck, Germany), in the 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 process, 0.5 wt.% boron (Merck, Germany) was added to steel powder to create a liquid phase during sintering. The binder for green strength was polyvinylalcohol (PVA), supplied by Merck, Germany. 2.5 wt.% PVA was added to the steel.

The mixture was compacted at 180 MPa into cylindrical specimens with a diameter of 12 mm and different heights. Green specimens were immersed in water at room temperature and ~90% of the carbamide was leached out in ~10 hours. Thermal debinding temperature of the PVA was determined to be 410 °C by using thermogravimetric analysis (TA, SDT Q600). The PVA in the green specimens was thermally removed as part of sintering cycle, which consisted of heating at a ramp rate of 5 °C/minutes to 410 °C (debinding) with a dwell time of 40 minutes, followed by heating at rate of 10 °C/minutes to sintering temperatures. The foams were sintered at 1260 °C for 40 minutes in H_2.

Kokubo's simulated body fluid and Hank's simulated body fluid were prepared from calculated amounts of chemicals supplied by Merck, Germany according to procedure described in the literature [12,13,18]. The amount of reagents for preparation of simulated body fluid solutions is given in Table 2.

In preparation of Kokubo's SBF solution, firstly 750 ml of distilled water was put into a 1000 ml beaker. The temperature was kept at ~37 °C. Reagents, which were listed in Table 2, were added into the water until the tris (tris-hydroxymethylaminomethane). The pH was measured and monitored using a pH meter (WTW, inoLab 720, Germany). After the addition of the tris, the temperature of the solution was checked, and the electrode (WTW, SenTix 81, Germany) of

Table 2
Reagents for preparation of Kokubo's and Hank's simulated body fluid solutions.

Reagent	Amount (g/l)	
	Kokubo's SBF solution	Hank's solution
NaCl	8.03	8.00
$CaCl_2$	0.29	0.14
KCl	0.22	0.40
$MgCl_2$ $6H_20$	0.31	0.10
K_2HPO_4 $3H_20$	0.23	–
KH_2PO_4	–	0.60
Na_2HPO_4 $2H_2O$	–	0.06
$MgSO_4$ $7H_2O$	–	0.06
$NaHCO_3$	0.35	0.35
Na_2SO_4	0.07	–
1.0 M HCl	39 ml	
Tris	6.11	–
1.0 M HCl	Appropriate amount	–
D-Glucose	–	1.00

the pH meter was placed in the solution. After the adjustment of pH, the solution was transferred from the beaker to a volumetric flask. Distilled water was added to the solution to adjust the total volume to 1000 ml. The pH of Kokubo's SBF is adjusted to 7.40 (human body condition), by adding 50 mM of tris and 45 mM of HCl. Solutions with pH values of 3.0 and 5.0 were also prepared to study the effect of pH on metal release. Preparation procedure of the Hank's solution was also included the similar steps. The reagents, which were listed in Table 2 for Hank's solution, were added to distilled water in the order they are listed. The pH of the solution was measured as 6.70.

The artificial saliva composition used in this study conformed to that described by Fusayama et al. [23,25] and the recipe is presented in Table 3. The pH of the prepared artificial saliva was 5.50. In addition, because the short-term pH variations of human saliva include the intake of acidic beverages (pH of ~2.0) and secretion of gastric acid (pH of ~1.0), lactic acid was also added to artificial saliva to decrease the pH to 2.30.

Seventy percent porous specimens were cut along longer axes and semi-cylindrical specimens were obtained. Thus, maximum solid surface area exposured to solution was obtained. Then, the specimens were machined and polished. Total porosity and surface area of each specimen was equal in immersion tests. Samples were then exposed to simulated body fluid and artificial saliva in closed polyethylene bottles. Foams with equal porosity levels were immersed in solutions at 37 °C for several soaking times up to 7 days. Solution volume to specimen surface area ratio was constant in all tests. The inductively coupled plasma-mass spectrometer, ICP-MS, (Thermo Scientific Elemental X Series 2) was employed to measure the concentrations of various metal ions like Fe, Cr, Ni, Cu and Mo which might be released. A solution without a specimen was used for the blank. After different soaking periods, foams were removed from the solutions. The dried specimens were weighed and the weight loss was determined. The area of the pores was subtracted from total surface area of the foams to find actual solid surface area.

The microstructure of foams was examined by scanning electron microscopy (SEM), Jeol 5600 and by optical microscope (Nikon, ME600). Energy dispersive spectroscopy (EDS) analysis was carried out to study the chemical composition (IXRF, 550i model EDS). The digital images

Table 3
Composition of artificial saliva solution.

Reagent	Amount (g/l)
NaCl	0.40
$CaCl_2$ $2H_2O$	0.79
KCl	0.40
NaH_2PO_4 $2H_2O$	0.78
Na_2S $9H_2O$	0.005
Urea–$CO(NH_2)_2$	1.00
Distilled water	1000 ml