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Comparison of metal release from various metallic biomaterials in vitro

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Abstract

To investigate the metal release of each base and alloying elements in vitro, SUS316L stainless steel, Co–Cr–Mo casting alloy, commercially pure Ti grade 2, and Ti–6Al–4V, V-free Ti–6Al–7Nb and Ti–15Zr–4Nb–4Ta alloys were immersed in various solutions, namely, α-medium, PBS(−), calf serum, 0.9% NaCl, artificial saliva, 1.2 mass% L-cysteine, 1 mass% lactic acid and 0.01 mass% HCl for 7 d. The difference in the quantity of Co released from the Co–Cr–Mo casting alloy was relatively small in all the solutions. The quantities of Ti released into α-medium, PBS(−), calf serum, 0.9% NaCl and artificial saliva were much lower than those released into 1.2% L-cysteine, 1% lactic acid and 0.01% HCl. The quantity of Fe released from SUS316L stainless steel decreased linearly with increasing pH. On the other hand, the quantity of Ti released from Ti materials increased with decreasing pH, and it markedly attenuated at pHs of approximately 4 and higher. The quantity of Ni released from stainless steel gradually decreased with increasing pH. The quantities of Al released from the Ti–6Al–4V and Ti–6Al–7Nb alloys gradually decreased with increasing pH. A small V release was observed in calf serum, PBS(−), artificial saliva, 1% lactic acid, 1.2% L-cysteine and 0.01% HCl. The quantity of Ti released from the Ti–15Zr–4Nb–4Ta alloy was smaller than those released from the Ti–6Al–4V and Ti–6Al–7Nb alloys in all the solutions. In particular, it was approximately 30% or smaller in 1% lactic acid, 1.2% L-cysteine and 0.01% HCl. The quantity of (Zr + Nb + Ta) released was also considerably lower than that of (Al + Nb) or (Al + V) released. Therefore, the Ti–15Zr–4Nb–4Ta alloy with its low metal release in vitro is considered advantageous for long-term implants.

Keywords: In vitro test; Corrosion; Metal release; Stainless steel; Cobalt–chromium–molybdenum alloy; Titanium alloy; pH

1. Introduction

Stainless steel, Co-based alloys and Ti materials are widely used implant materials in clinical practice with each material having its own advantages. Since the metal release from implants is an important subject, numerous studies, including long-term clinical studies, have been conducted on metal release from orthopaedic implants into body fluids (serum, urine, etc.) [1–12]. The toxic effects of metals released from prosthetic implants have been reviewed [1]. Implant components fabricated from Co-based alloys have been reported to produce elevated Co, Cr and Ni concentrations in body fluids [3–5,10]. Significantly elevated metal concentrations in body fluids of patients with Co–Cr alloy metal-on-metal bearing hip implants have been reported [4,7,8]. Ti–6Al–4V alloy has been employed for implants and the cytotoxicity of V has become an issue of concern [1,12,13–16]. Therefore, many studies on metal release from Ti–6Al–4V alloy and on surface treatments that reduce the quantity of V released have also been reported [17–19].

Metals from orthopaedic implants are released into surrounding tissue by various mechanisms, including corrosion, wear, and mechanically accelerated electrochemical processes such as stress corrosion, corrosion fatigue and fretting corrosion. This metal release has been associated with clinical implant failure, osteolysis, cutaneous allergic reactions, and remote site accumulation [9,11].

The increase in the incidence of allergy, and the necessity for prolonged use require implants having less metal release. In particular, in selecting suitable

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Table 1
Chemical composition (mass%) of materials used

	Cr	Ni	Mo	Mn	C	Si	P	S	Cu	Fe	Co	
SUS316L	17.00	13.0	2.25	1.40	0.024	0.82	0.025	0.009	0.5	Bal.	—	
Co–Cr–Mo casting alloy	28.36	0.3	6.1	0.42	0.27	0.63	—	—	—	0.46	Bal.	
Titanium alloys	Zr	Nb	Ta	Pd	Al	V	Fe	O	N	H	C	Ti
CP Ti grade 2	—	—	—	—	—	—	0.050	0.101	0.0049	—	—	Bal.
Ti–6Al–4V	—	—	—	—	6.25	4.28	0.214	0.081	0.003	0.0063	—	Bal.
Ti–6Al–7Nb	—	6.55	0.01	—	5.97	—	0.22	0.18	0.01	0.0035	0.01	Bal.
Ti–15Zr–4Nb–4Ta	14.83	3.97	4.01	0.16	—	—	0.04	0.22	0.05	0.0057	0.01	Bal.

materials on the basis of usage conditions and durations, the behavior of metal release from each base and alloying element constituting the metallic biomaterials should be examined using various solutions simulated human body fluids. However, there are insufficient research studies that adequately compare metal release from implant materials using various media under the same experimental conditions. In this study, we conducted static immersion tests using various implant materials to obtain quantitative data required for choosing suitable materials according to various clinical usage conditions and durations, and for selecting the optimum test solution to simulate the body environment. Stainless steel, Co–Cr–Mo alloy, and Ti materials were immersed under the same conditions in α-medium, PBS(−), calf serum, 0.9% NaCl, artificial saliva, 1.2 mass% L-cysteine, 1 mass% lactic acid and 0.01 mass% HCl solutions at 37°C for 7 d. Moreover, the metal release of each base and alloying element was compared with pH.

2. Experimental materials and methods

2.1. Alloy specimens

SUS316L stainless steel, which is used for the manufacture of surgical implants in Japan, specified in the Japanese Industrial Standard (JIS) G 4303 was melted by vacuum-induction melting. After soaking at 1200°C for 3 h, the ingot was forged. The billet soaked at 1200°C for 1 h was hot-worked. After maintaining at 1050°C for 30 min, the plate was quenched in water. Finally, the stainless steel plate was solution-treated at 1050°C for 2 min, and then quenched in water. The Co–Cr–Mo alloy specified in ISO 5832-4 was subjected to vacuum-induction melting, and then vacuum-cast by pouring at 1420°C into a mold manufactured by lost wax process. The ingot was homogenized at 1220°C for 4 h. The Co–Cr–Mo alloy as cast (Co–Cr–Mo casting alloy) was used in the immersion test. Commercially pure Ti (CP Ti) grade 2 (ISO 5832-2), the Ti–6Al–4V alloy (ISO 5832-3), the Ti–6Al–7Nb alloy (ISO 5832-11), and the Ti–15Zr–4Nb–4Ta alloy currently specified for surgical implants in JIS T 7401-4 were subjected to vacuum-arc melting. After β (after soaking: 1100°C-3 h for CP Ti, 1150°C-3 h for Ti–6Al–4V and Ti–6Al–7Nb, 1050°C-4 h for Ti–15Zr–4Nb–4Ta) and $\alpha-\beta$ forging (starting temperature: 850°C for CP Ti, 930°C for Ti–6Al–4V and Ti–6Al–7Nb, 750°C for Ti–15Zr–4Nb–4Ta), the Ti materials except for the Ti–6Al–7Nb alloy were annealed for 2 h at 700°C. The Ti–6Al–7Nb alloy was annealed for 2 h at 740°C. The chemical compositions of stainless steel, the Co–Cr–Mo casting alloy and Ti materials are shown Table 1.

2.2. Static immersion test

The static immersion test was performed in accordance with the currently specified JIS T 0304 standard for metallic biomaterials. Plate specimens ($n = 25$), each $20 \times 40 \times 1\,mm^3$, were cut from each alloy specimen. Immersion tests were conducted at 37°C using various solutions, namely,α-medium (α-modified Eagle's medium, manufactured by Dainippon Pharmaceutical Co. Ltd., containing NaCl, 6.8 g; KCl, 0.4 g; Na_2HPO_4, 1.15 g; $NaH_2PO_4 \cdot H_2O$, 0.2 g/l; and trace amounts of amino acids and vitamins, pH = 7.4); α-medium containing 10 vol% fetal bovine serum (Gibco BRL, Div. of Life Tech. Inc.) and 7.5% $NaHCO_3$ solution (1 vol%), phosphate-buffered saline (PBS(−) produced by Nissui Pharmaceutical Co. Ltd., Japan, containing NaCl, 8 g; KCl, 0.2 g; NaH_2PO_4, 0.14 g; and KH_2PO_4, 0.2 g/l, pH = 7.2), membrane-filtered calf serum (Gibco BRL, Div. of Life Tech. Inc., pH = 6.9), 0.9 mass% NaCl (prepared using guaranteed reagents manufactured by Nacalai Tesque, Inc., Japan, pH = 6.6), artificial saliva (manufactured by Teijin Pharma Ltd., Japan, containing NaCl, 0.844 g; KCl, 1.2 g; $CaCl_2$, 0.146 g; $MgCl_2$, 0.052 g; K_2PO_4, 0.342 g/l; and small amounts of thickener and benzoic acid, pH = 6.2, viscosity: 6 mPa s), 1 mass% lactic acid (prepared with guaranteed reagents manufactured by Nacalai Tesque, Inc., Japan, pH = 2.6), 1.2 mass% L-cysteine (pH = 2.1)-simulated amino acid, and 0.05 vol% concentrated HCl (0.01 mass% HCl, pH = 2.0). The 1.2 mass% L-cysteine