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Biocompatibility of corrosion-resistant zeolite coatings for titanium alloy biomedical implants

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Abstract

Titanium alloy, Ti6Al4V, is widely used in dental and orthopedic implants. Despite its excellent biocompatibility, Ti6Al4V releases toxic Al and V ions into the surrounding tissue after implantation. In addition, the elastic modulus of Ti6Al4V (∼110 GPa) is significantly higher than that of bone (10–40 GPa), leading to a modulus mismatch and consequently implant loosening and deosteointegration. Zeolite coatings are proposed to prevent the release of the toxic ions into human tissue and enhance osteointegration by matching the mechanical properties of bone. Zeolite MFI coatings are successfully synthesized on commercially pure titanium and Ti6Al4V for the first time. The coating shows excellent adhesion by incorporating titanium from the substrate within the zeolite framework. Higher corrosion resistance than the bare titanium alloy is observed in 0.856 M NaCl solution at pHs of 7.0 and 1.0. Zeolite coatings eliminate the release of cytotoxic Al and V ions over a 7 day period. Pluripotent mouse embryonic stem cells show higher adhesion and cell proliferation on the three-dimensional zeolite microstructure surface compared with a two-dimensional glass surface, indicating that the zeolite coatings are highly biocompatible.

Keywords: Corrosion resistant; Biocompatible; Zeolite; Biomaterial; Stem cells

1. Introduction

The most essential properties of a biomedical implant, such as a total joint replacement, include biocompatibility, corrosion resistance and an elastic modulus that closely matches that of the human bone to avoid bone resorption [1–3]. At present, titanium alloy, Ti6Al4V, is the material most widely used for these implant applications because it is readily available and has reasonable biocompatibility and corrosion resistance and a relatively low modulus when compared to other alloys, such as stainless steel and cobalt chromium alloys [4]. However, Ti6Al4V still releases vanadium and aluminum ions [5–7], causing poor osteointegration and a limited lifespan of the titanium prosthesis. Vanadium ions are cytotoxic, while aluminum ions can cause neurological disorders [8–10]. To prevent or reduce the release of harmful ions, ceramic and polymer coatings have been applied [5], but below-par material properties and poor adhesion of these biocoatings to the metal substrate have led to their failure. In addition, although the elastic modulus of Ti6Al4V (∼110 GPa) [11] is among the lowest of metal alloys used for implant applications, it is still much higher than that of the bone (∼30 GPa) [12], leading to bone resorption. To avoid the release of harmful ions and to reduce the elastic modulus, highly sophisticated titanium alloys (e.g., TiNbZr) have been developed, but they are expensive.

Zeolites are aluminosilicates with a uniform microporous structure, and have been exploited commercially for catalysis and separation processes [13]. Researchers have shown zeolites to be non-toxic, viable carriers, controlled

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release agents and adjuvants for drugs, thus showing their potential for biomedical applications [12–19]. While zeolites are used in composite powder form for catalysis and separation applications, high-silica zeolite coatings have previously been prepared on aluminum alloys and shown to be highly resistant to corrosion [20]. Zeolite coatings act as a barrier between metal and corrosive medium to prevent corrosion. In addition, zeolite coatings have been shown to have an elastic modulus of 30–40 GPa [21], which much more closely matches that of a bone than titanium alloys [22].

In this study we show that a high-silica zeolite MFI[1] coating can be deposited on titanium alloys to prevent the dissolution of the underlying metal, thus eliminating the release of harmful ions. More importantly, we demonstrate that zeolite coatings are biocompatible and can better sustain the growth of mouse embryonic stem cells (mESC) on a fibroblast feeder layer than glass.

2. Materials and methods

2.1. Substrate and substrate pretreatment

Commercially pure titanium (cpTi, 99.5%, 0.25 mm thick; Alfa Aesar, Ward Hill, MA) and high strength titanium (Ti6Al4V, 6% Al, 4% V, 0.41 mm thick; McMaster Carr, Cleveland, OH) were purchased. The substrates were sized to 15.25×7.62 cm panels and immersed at 70 °C for 1 h in an Alconox® detergent solution prepared with 3.0 g of Alconox® (Sigma–Aldrich, St. Louis, MO) in 400 ml of deionized (DI) H_2O. The substrates were then rinsed under DI H_2O with mild rubbing. Substrates were dried with compressed air and kept at ambient conditions for less than 1 h before immersion in HSZ-MFI synthesis solution.

2.2. Coating solution formulation

High-silica zeolite (HSZ) MFI coatings were prepared by an in situ crystallization method. First, a clear synthesis solution with a molar composition of 0.16TPAOH:0.64NaOH:1TEOS:92H_2O:0.0018Al (weight compositions: 17.03 g TPAOH, 5.36 g NaOH, 43.60 g TEOS, 336.00 g H_2O, 0.0105 g Al) was prepared by dissolving aluminum powder (200 mesh, 99.95+ wt.%; Aldrich, St. Louis, MO) in sodium hydroxide (99.99 wt.%; Aldrich) and DI H_2O followed by the dropwise addition of tetrapropylammonium hydroxide (TPAOH, 40 wt.%, aqueous solution; SACHEM, Austin, TX) and tetraethylorthosilicate (TEOS, 98 wt.%; Sigma–Aldrich, St. Louis, MO) under stirring. The clear solution was aged at room temperature for about 4 h under stirring before use.

2.3. Coating deposition

A 2 l Teflon-lined Parr autoclave (Model # 4622, Parr Instruments, Moline, IL) was used as the synthesis vessel and the substrate was suspended vertically inside the synthesis solution using a Teflon® holder and steel wire. Crystallization was carried out in a convection oven at 175 °C for 24 h, after which the autoclave was removed from the oven and quenched with tap water. The coated sample was rinsed with DI H_2O and dried in ambient room air before characterization.

2.4. Physico-chemical characterizations

Scanning electron microscopy (SEM) micrographs were obtained on a Philips XL30-field emission gun scanning electron microscope operated at between 5 and 20 kV. An Au/Pd coating was applied to MFI-coated cpTi and Ti6Al4V samples by sputtering for 20 s before SEM imaging. Adhesion of the coating to cpTi and Ti6Al4V substrates was determined according to ASTM Test Method D 3359, using PAT-2000 adhesion test kit (Paul N. Gardner Co., Pompano Beach, FL). Following a scratch test, the coating is visually inspected and rated on a scale of 0–5, with 5 being the highest rating. A focused ion beam (FIB; Leo XB1540), equipped with a gallium ion gun, was used to mill a 15 μm deep trench in the zeolite–titanium system. Incorporation of titanium in the zeolite structure was determined by semi-quantitative energy-dispersive X-ray spectroscopy (EDS), using the EDAX (Mahwah, NJ) analytical system attached to the FIB column. X-ray diffraction (XRD) measurements were done on bare and MFI-coated cpTi and Ti6Al4V using a Bruker AXS (Madison, WI) D8 Advance Diffractometer using Cu K_α radiation.

2.5. Corrosion resistance

Large coated substrates were cut into 2.5×3.8 cm coupons for direct current (DC) polarization tests. Before immersing the coupons into corrosive medium, the edges of the coated substrate were sealed with five-min epoxy (Grainger, Riverside, CA) while exposing the coating surface on which corrosion-resistance was to be measured. Polarization testing was carried out with a Solartron (Farnborough, Hampshire, UK) potentiostat SI 1287 in a three-electrode configuration, with the zeolite-coated substrate as the working electrode, a platinum foil as the counter electrode and an Ag/AgCl-saturated KCl electrode as the reference electrode. The corrosive medium was either 0.856 M NaCl (pH 7.0) or 0.856 M NaCl/HCl (pH 1.0) aqueous solution. Zeolite-coated samples were immersed in the corrosive medium for 0–7 days prior to the polarization test (note that immersion for a few minutes up to 30 min is normally employed by others for corrosion testing). Ambient temperature was maintained during all polarization tests. A scan rate of 1 mV s^{-1} was applied

[1] MFI is a three-letter code assigned to the zeolite used in this study by the International Zeolite Association.