Surface Modification of Equiatomic Nitinol Alloy to Reduce Ni Ion Release

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Introduction: Nitinol, an equal-atomic Ni and Ti alloy (NiTi), can be classified as a new biomaterial. Among many metallic materials, Nitinol is gaining more attention due to its excellent biocompatibility comparable to or better than Ti in combination with shape memory effect and superelasticity. Nitinol alloy has a low elastic modulus between 20 to 90 GPa, which is closer to that of dense (cortical) bone (between 15 to 25 GPa). The biocompatibility of NiTi and its unusual mechanical properties make it an ideal engineering material for variety of bone implant applications. However, the release of Ni in to the human body is considered to be a serious problem with NiTi implants, as Ni is known to be allergenic and carcinogenic, though essential for the human body. A great deal of research efforts has been made on Nitinol surface modifications and coatings.

Methods: In this study, the surface of Laser Engineered Net Shaping (LENS™) processed NiTi alloy has been modified using anodization in H_2SO_4 electrolyte with varying pH at 20V. The influence of anodization on *in vitro* cell-materials interactions and Ni release of NiTi alloy is studied in detail.

Dense cylindrical NiTi alloy samples with 7 mm diameter and 40 mm height were made using 350 W laser power, 13 mm/s scan speed and a powder feed rate of 5.5 g/min. The cylindrical samples were removed from the substrate and disc samples of 2 mm thick were then cut from the cylindrical samples using a water jet. The disc samples were abraded by silicon carbide paper in successive grades of 400, 600, and 1200 grit then ultrasonically cleaned in distilled water and dried at room temperature. Final polishing was done using a cotton polishing cloth with a 0.5μm alumina suspension. For the anodization process, a NiTi alloy anode was suspended on one side of the cell and a platinum cathode ($1cm^2$) was suspended on the other side. Both anode and cathode were connected to the power supply by platinum wires and a thermometer was placed in the beaker. A DC power supply was used for the applied voltage. 1 (N) sulfuric acid (H_2SO_4) was used as electrolytic solution was prepared by dissolving 0.42 g of citric acid and 0.42 g of NaF in a solution containing 5.5. mL H_2SO_4 and 94.5 mL distilled H_2O. Electrolyte with three different pHs (4.5, 2.0 and 1.5) was achieved by adding either HCl or NaOH. All anodization experiments were performed at 20V for different durations at 15 minute increments up to 1h. To evaluate the influence of microtexturing of Nitinol surface via anodization on surface wettability, contact angles were measured using the sessile drop method on a face contact angle set-up equipped with a microscope and a camera. Nickel ion release was measured in simulated body fluid. A Shimadzu Atomic Absorption spectrometer (AA-6800, Columbia, MD) in the graphite furnace mode was used to determine the Ni concentration in the SBF as a function of time. For the cell–materials interaction studies, human fetal osteoblast (hFOB) cells, CRL-11372 (ATCC, VA, USA) were used. Samples were then removed from culture at 3, 7 and 11days of incubation to study cell–materials interactions under FESEM.

Results: Anodization of NiTi alloy resulted in micro/nano textured surfaces with varying asperities. Close inspection of anodized surface features showed that both the electrolyte pH and anodization time strongly influence the surface morphologies. This process produced porous surfaces on the order of micron and nanometer sized pores. Comparison of surface morphology of NiTi alloy anodized in an electrolyte with a pH of 4.5 for 15 min to that of surface anodized for 30 min indicate that surface asperities such as pits/pores not only grow in number but also in size covering the entire surface of the sample. There is almost an order of magnitude difference in roughness for the as-process NiTi alloy and anodized surfaces. As-processed and polished NiTi alloy samples show a smooth surface with an r.m.s roughness value of 0.008μm, which increased to a maximum value of 0.075 μm for the surface anodized for 60 min. in an electrolyte with pH 1.5.

All the samples showed well spread and flattened cell morphologies after 7 days of culture period. However, anodized samples clearly produced cells adhering to each other with cellular micro extensions (e.g. filopodia) and were connected to the substrate in addition to the neighboring cells. Anodization of NiTi alloy can increase the corrosion resistance by forming oxide layer that acts as a barrier layer to prevent Ni^{2+} ions from leaching out of the bulk material. We found that anodization significantly reduced Ni release from NiTi alloy surface. However, all the Nitinol surfaces showed more or less similar and gradual Ni release, and none of the surfaces exhibited saturation or plateau in the Ni release.

Conclusions: Anodization treatment was successfully applied to laser processed NiTi alloy to improve cell-materials interactions and also to reduce Ni ion release and associated allergic and toxic reactions. A significant drop in Ni ion release from 268 to 136 ppb has been observed for NiTi surfaces after anodization.