Nitinol modified by calcium phosphate coatings prepared by sol-gel method and electrodeposition

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Nitinol, the titanium-nickel alloy, has been widely used in the field of orthopedic surgery owing to its unique properties, such as shape memory effect, superelasticity, and high damping capacity [1]. Although Nitinol possess high corrosion resistance in physiological solutions caused by the spontaneously formed passive film of TiO_2, the major concern regarding its biocompatibility is release of allergenic and toxic Ni^{2+} ions due to *in vivo* corrosion. To prevent nickel dissolution, Nitinol has been modified using different surface treatments [2]. In the present work, the Nitinol surface was modified with calcium phosphate (CaP) ceramic coatings. This method of protection combines good mechanical properties of the metallic substrate with good biocompatibility of CaP [3].

CaP coatings on the Nitinol surface were formed using two low-temperature methods: sol-gel and electrodeposition. The CaP coatings were deposited on Nitinol from the sol consisting of calcium 2-ethylhexanoate and 2-ethylhexyl-phosphate as calcium and phosphorous precursors, respectively. The coatings were subsequently dried and calcined at 450 and 600 °C. Electrodeposition of hydroxyapatite (HAp) was performed potenciostatically from solution containing 0.1 M $Ca(NO_3)_2$ and 0.06 M $NH_4H_2PO_4$.

The morphology and microstructure of CaP coatings were characterized by field emission scanning electron microscopy (SEM). The chemical composition was examined using energy dispersive X-ray spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction analysis (XRD). The barrier properties of coatings were tested in a physiological Hanks' solution using electrochemical impedance spectroscopy (EIS). The influence of calcination temperature and multilayer structure on morphological, structural and barrier properties of sol-gel coatings was determined.

The single-layer sol-gel coatings showed cracked morphology due to different thermal expansion coefficients of the Nitinol substrate and the CaP coating. In contrast, multi-layer coatings were homogeneous and dense, as a result of the coating densification during the calcination. The electrodeposited coatings were homogenous and dense consisting of needle-like crystals.

The XRD, FTIR and EDS data have shown that sol-gel method results in formation of biphasic CaP ceramic consisting of HAp and tricalcium phosphate (TCP) with small amount of calcite. The EDS analysis of electrodeposited films showed the HAp coating was obtained.

Additionally, the early stage of HAp electrocrystallization on Nitinol was studied using cyclic voltammetry (CV) and chronoamperometry (CA). The HAp nucleation is three-dimensional progressive nucleation under diffusion control.

Both sol-gel CaP and electrodeposited HAp coatings offer excellent corrosion protection and act as an effective barrier between Nitinol and the aggressive environment, which prevents transport of allergenic nickel ions into bio environment.

Figure 1 shows impedance spectrum of sol-gel derived CaP coated Nitinol recorded in simulated physiological solution. High impedance modules, $|Z|$, the value order of 10^8 Ωcm^2, are characteristic for the blocking electrode|solution interface. For comparison, the $|Z|$ value of Nitinol coated with native oxide film is 2 orders of magnitude lower.

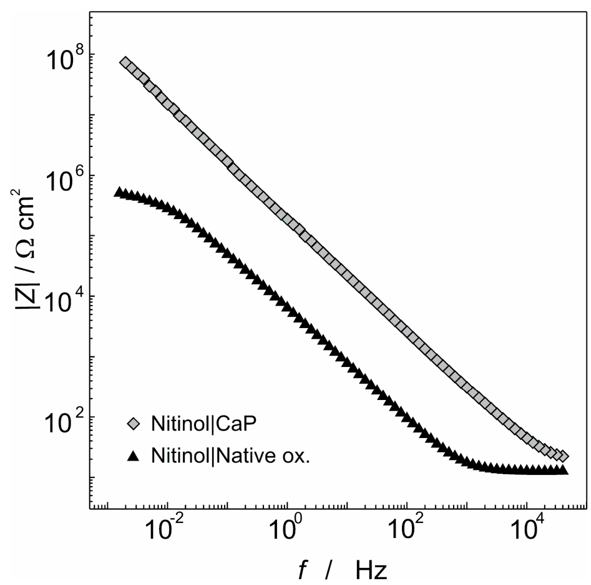

Figure 1. Impedance spectra of uncoated and CaP coated Nitinol recorded in Hanks' solution (37 °C).

There are still many open questions regarding the area of calcium phosphate chemistry, thus we believe that results presented will lead to better understanding and development of biocompatible CaP coatings on metal implants.

References:

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