ZrO_2 hybrid sol-gel coatings for active corrosion protection of Ti6Al4V biomedical alloy in simulated body fluids

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Interactions of simulated body environments with ZrO_2 hybrid sol-gel coatings deposited on Ti6Al4V biomedical alloy samples were studied by applying advanced electrochemical techniques.

The preparation of the sol-gel thin films was made by mixing two organopolysiloxane precursors and a zirconia precursor: γ-methacryloxypropyltrimethoxysilane (MAPTMS), as organic precursor; tetramethoxysilane (TMOS) as inorganic precursor, and zirconium tetrabutoxide (ZTB), with the aim to incorporate ZrO_2 nanoparticles into the hybrid sol-gel network. Sols were prepared starting from mixtures of 4 mols of MAPTMS and 1 mol of TMOS. Finally the zirconia precursor was added to yield a 1%wt ZrO_2. Ethanol (EtOH) was used as solvent and the stoichiometric water for the complete hydrolysis was added for all the compositions prepared. Acetic acid (HAc) was employed as a catalyst. ZTB undergoes a very fast hydrolysis in an aqueous-alcoholic solution, usually resulting in flocculation and precipitation of the zirconia source. The addition of a small volume of acetylacetone (Hacac) before the addition of HAc and deionised water allows Zr^{4+}-ions to remain co-ordinated. In this case the hydrolysis rate of the zirconia source is diminished. Sol-gel thin films on Ti6Al4V biomedical alloy substrates were obtained by dip-coating.

The effects of ZrO_2 content on the thermal stability of the prepared hybrids were investigated by using thermal analysis (TG/DTG). Structural characterization of the coatings was carried out using attenuated total reflectance Fourier transformer infrared spectroscopy (ATR-FTIR). Contact angle measurements were used to study the hydrophilicity of the coatings. The thickness of the MAPTMS/TMOS/ZrO_2 coatings was measured by using a profilemeter. Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDX) has been applied to study the surface morphology and composition of the MAPTMS/TMOS/ZrO_2 coatings.

The corrosion protection behaviour of the sol-gel coatings was analysed with global and local electrochemical impedance spectroscopies (EIS/LEIS) and scanning vibrating electrode techniques (SVET) after applying soaking tests of the coating/Ti6Al4V alloy system in Kokubo's simulated body fluid (SBF) for variable immersion time.

SEM analysis before soaking in SBF showed the formation of a uniform, homogeneous, crack free and highly adherent protective film on the substrates. SEM/EDX analysis after 4 days of immersion in SBF showed the accumulation of bone-like apatite precipitated on the sol-gel coating. Previous studies have shown that the application of these hybrid ZrO_2/organopolysiloxane films on Ti6Al4V alloy also produces an enhanced fibrinogen protein adsorption compared with pure organopolysiloxane films [1]. Electrochemical analyses show that the incorporation of ZrO_2 in MAPTMS-TMOS improves the corrosion protection of these sol-gel coatings. These promising results suggest the possible use of these coating/Ti6Al4V systems as potential materials for clinical implantation purposes.

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References
[1] A.A. El hadad, V. Barranco, A. Jiménez-Morales J.C. Galván, C.C. Perry, *paper in preparation*.