

Optimization of anodization process of AZ31 alloys for biomedical applications

Andrea Zaffora*, Danilo Virtù, Francesco Di Franco and Monica Santamaria

Dipartimento di Ingegneria, Università degli Studi di Palermo, Viale delle Scienze, 90128 Palermo, Italy

*andrea.zaffora@unipa.it

Metallic materials are widely used for biomedical applications, as repair or replacement materials of the diseased or damaged bone tissue. Compared with traditionally employed stainless steels, titanium alloys and Cr-Co based alloys, magnesium and its alloys show special properties, such as a low density ($1.74 - 2.0 \text{ g cm}^{-3}$), an elastic modulus between 41 and 45 GPa, very well matching with that of natural bone. And last but not least, once implanted in vivo the ions and/or particles released as a consequence of corrosion as well as wear processes are not harmful to the body [1]. Therefore, magnesium and its alloys are candidate materials for biodegradable implants for orthopedic applications and vascular stents [2, 3]. However, due to the very low reduction potential and to the poor corrosion resistance in chloride containing environments (as human body fluids or blood plasma), the degradation rate of magnesium and its alloys is so high that the mechanical integrity before the diseased or damaged bone tissue healed is not always maintained. Moreover, since water reduction is the common cathodic process during corrosion of Mg and its alloys, the high corrosion rate implies a high H_2 evolution rate, with consequent detrimental gas pockets formation around the implant, and alkalization occurring in the vicinity of the corroding surface discussed as possibly being deleterious for the surrounding biological environment [4].

The simplest way to slow down corrosion is to form a coating on the magnesium/magnesium alloy substrate to provide a barrier toward the contact between the substrate and the environments. There are many coating technologies that can be used, such as electrochemical plating, chemical conversion coating, physical vapour deposition, laser surface treatment and anodic oxidation. Among these technologies, the latter is one of the most effective and popular methods, even if the growth of protective anodic layers on Mg and Mg alloys is difficult due to the unfavorable Pilling-Bedworth ratio for MgO .

In the present work, the anodization of AZ31 alloy was carried out in hot glycerol (HG) electrolyte containing K_2HPO_4 and K_3PO_4 in the attempt to induce the growth of a magnesium phosphate protective layer on the surface of AZ31 with a more favourable PBR than that of MgO . We optimized anodization process conditions (e.g. bath temperature, current density, anodization time) in order to improve corrosion resistance of metallic substrate. Moreover, in the attempt to seal the pores of the anodic layers and to improve their biocompatibility, the growth of Hydroxyapatite (HAP) on the samples surface was induced by a dip coating procedure. The structure and composition of the resultant films was studied by Scanning Electron Microscopy, Energy Dispersive X-ray Spectroscopy and Raman Spectroscopy. The corrosion resistance of the resulting composite coatings was characterized in Simulated Body Fluid at 37°C by Open Circuit Potential (OCP) measurements, Electrochemical Impedance Spectroscopy (EIS) and by recording polarization curves. Accurate measurement of the hydrogen evolution was obtained and in vitro studies were carried out to evaluate the cytocompatibility of the anodized AZ31 samples.

[1] L. Zhao, C. Cui, Q. Wang, S. Bu, *Corros. Sci.* 52 (2010) 2228-2234.

[2] M.P. Staigera, A. M. Pietaka, J. Huadmai, G. Dias, *Biomaterials* 27 (2006) 1728-1734.

[3] B. Heublein, R. Rohde, V. Kaese, M. Niemeyer, W. Hartung, A. Haverich, *Heart* 89 (2003) 651-656.

[4] M. Esmaily, J.E. Svensson, S. Fajardo, N. Birbilis, G. S. Frankel, S. Virtanen, R. Arrabal, S. Thomas, L.G. Johansson, *Prog. Mater. Sci.* 89 (2017) 92-193.