Modification of the magnesium corrosion rate in physiological saline 0.9 wt % NaCl via chemical and electrochemical coating of reduced graphene oxide

J.M. Molina[1], J. Fernández[2], Y. El Ouardi[2], J. Bonastre[2], F. Cases[2]

[1]Departamento de Química Inorgánica de la Universidad de Alicante e Instituto Universitario de Materiales de Alicante, University of Alicante, Ap 99, E-03080 Alicante, Spain
[2]Departamento de Ingeniería Textil y Papelera, Escuela Politécnica Superior de Alcoy, Universitat Politècnica de València, Plaza Ferrándiz y Carbonell, s/n, 03801 Alcoy, Spain

[1](J.M. Molina) jmmj@ua.es; [2](F. Cases) fjcases@txp.upv.es

Abstract (Arial 10)

Different metallic materials have been used as biomaterials for the manufacture of medical implants. Commonly used metallic biomaterials include stainless steel, pure titanium, titanium-aluminum-vanadium-based alloys and cobalt-chromium-molybdenum-based alloys [1–5]. The advantages of biodegradable Mg-based implants [6–8] lie in their mechanical and electrochemical properties. Mg is a lightweight metal with a density of 1.74 g cm −3 versus 7.9 g cm −3 for Al and 4.5 g cm −3 for Ti. Moreover, Mg presents an elastic modulus and compressive yield strength closer to those of natural bone [9]. In addition, Mg is a biocompatible material naturally found in the human body (approximately half of the total physiological Mg is stored in the bone tissue) [10]. Setbacks when using Mg as metallic material for biomedical applications are related to its low corrosion resistance under the physiological conditions [9] and the excessively rapid production of hydrogen gas during the in-vivo corrosion [11]. The first issue could lead to both a rapid loss of its mechanical properties and severe problems in tissue regeneration, and the second, to harmful effects during the tissue healing process. One of the most recent studies dedicated to slowing down the dissolution of magnesium in saline conditions was performed on samples of magnesium foam manufactured using the replication method from carbon spheres as a template. The heat treatment in air flow at 540 °C applied to burn the template particles generated a layer of oxide on the surface of the foam which notably slowed down its dissolution at 37 °C in an aqueous solution containing 3 wt % NaCl that had a pH of 7.4 (a pH closed to that of the human body) [12]. Other surface modifications that were proved to be successful in slowing the corrosion rate of magnesium were fluoride conversion coatings, phosphate treatments or chemical deposition of hydroxyapatite and octacalcium phosphate [13].
Moreover, it has been proved that both graphene oxide (GO) and reduced graphene oxide (RGO) show anti-corrosion properties when coated onto metal substrates [14–19]. The syntheses of the different graphene-metallic substrate specimens were carried out following both electrochemical [20–22] and chemical [23,24] methods.

The synthesis of reduced graphene oxide onto magnesium discs by electrochemical and chemical methods is presented in this work. The surface morphology and atomic composition were investigated using field emission scanning electron microscopy and energy dispersive X-ray spectroscopy. The corrosion rate of different samples was analyzed in physiological saline 0.9 wt % NaCl solution by potentiodynamic polarization, electrochemical impedance spectroscopy and scanning electrochemical microscopy. As a result of the different treatments, a progressive decrease in the corrosion rate of the magnesium disc in the corroding environment was obtained, reaching up to 80% of reduction for the chemically modified sample.

References

[1] U. Zwicker, K. Buhler, R. Muller, H. Beck, H.J. Schmid, J. Ferstl, Mechanical properties and tissue reactions of a titanium alloy for implant material, in: I. Kimura (Ed.), Titanium'80, Science and Technology, vol. 1, Metallurgical Society of AIME, New York, NY, USA, 1980, pp. 505–514.

[2] B.P. Bannon, E.E. Mild, Titanium Alloys for Biomaterial Application: An Overview. Titanium Alloys in Surgical Implants, ASTM, Philadelphia, PA, USA, 1983, pp. 7–15.

[3] M. Long, H.J. Rack, Titanium alloys in total joint replacement −A materials science perspective, Biomaterials 19 (1998) 1621–1639.

[4] M. Niinomi, Recent metallic materials for biomedical applications, Metall. Mater.

[9] M.P. Staiger, A.M. Pietak, J. Huadmai, G. Dias, Magnesium and its alloys as orthopedic biomaterials: a review, Biomaterials 27 (2006) 1728–1734.

[10] Merck Manual of Diagnosis and Therapy (online): Section 2: Endocrine & Metabolic Disorders, Chapter 12: Water, Electrolyte, Mineral, And Acid-Base Metabolism, seventeenth ed., (2019).

[11] F. Witte, V. Kaese, H. Haferkamp, E. Switzer, A. Meyer-Lindenberg, C.J. Wirth, et al., In vivo corrosion of four magnesium alloys and the associated bone response, Biomaterials 26 (2005) 3557–3563.

[12] J.M. Ferri, J.M. Molina, E. Louis, Fabrication of Mg foams for biomedical applications by means of a replica method based upon spherical carbon particles, Biomed. Phys. Eng. Express 1 (2015) 045002.

[13] T.S.N. Sankara, I.S. Park, M.H. Lee (Eds.), Surface Modification of Magnesium and Its Alloys for Biomedical Applications, Woodhead Publishing, 2015.

[14] N.T. Kirkland, T. Schiller, N. Medhekar, N. Birbilis, Exploring graphene as a corrosion protection barrier, Corros. Sci. 56 (2012) 1–4.

[15] B.P. Singh, S. Nayak, K.K. Nanda, B.K. Jena, S. Bhattacharjee, Laxmidhar Besra, The production of a corrosion resistant graphene reinforced composite coating on copper by electrophoretic deposition, Carbon 61 (2013) 47–56.

[16] B. Ramezanzadeh, A. Ahmadi, M. Mahdavian, Enhancement of the corrosion protection performance and cathodic delamination resistance of epoxy coating through treatment of steel substrate by a novel nanometric sol-gel based silane composite film filled with functionalized graphene oxide nanosheets, Corros. Sci. 109 (2016) 182–205.

[17] K. Qi, Y. Sun, H. Duan, X. Guo, A corrosion-protective coating based on a solutionprocessable polymer-grafted graphene oxide nanocomposite, Corros. Sci. 98 (2015) 500–506.

[18] B. Ramezanzadeh, S. Niroumandrad, A. Ahmadi, M. Mahdavian, M.H. Mohamadzadeh Moghadam, Enhancement of barrier and corrosion protection performance of an epoxy coating through wet transfer of amino functionalized graphene oxide, Corros. Sci. 103 (2016) 283–304.

[19] Z. Yang, W. Sun, L. Wang, S. Li, T. Zhu, G. Liu, Liquid-phase exfoliated fluorographene as a two dimensional coating filler for enhanced corrosion protection performance, Corros. Sci. 103 (2016) 312–318.

[20] J. Zhao, X. Xie, Ch. Zhang, E*ff*ect of the graphene oxide additive on the corrosion resistance of the plasma electrolytic oxidation coating of the AZ31 magnesium alloy, Corros. Sci. 114 (2017) 146–155.

[21] F. Wu, J. Liang, W. Li, Electrochemical deposition of Mg(OH) 2 /GO composite films for corrosion protection of magnesium alloys, J. Magnesium Alloys 3 (2015) 231–236.

[22] X.Z. Deng, Y.W. Wang, J.P. Peng, K.J. Liu, N.X. Feng, Y.Z. Di, Surface area control of nanocomposites Mg(OH) 2 /graphene using cathodic electrodeposition process: high adsorption capability of methyl orange, RSC Adv. 6 (2016) 88315–88320.

[23] M. Heidarizad, S.S. Sengör, Synthesis of graphene oxide/magnesium oxide nanocomposites with high-rate adsorption of methylene blue, J. Mol. Liq. 224 (2016) 607–612.

Trans. A 33 (2002) 477–486.

[24] L. Baojun, H. Cao, G. Yin, Mg(OH) 2 @reduced Graphene oxide composite for removal of dyes from water, J. Mater. Chem. 21 (2011) 13765–13768.