

In vitro Degradation and Corrosion Evaluation of Mg-Ca Alloys for Biomedical Applications

A.I. BITA^a, A. ANTONIAC^a, C. COTRUT^a, E. VASILE^b, I. CIUCA^a, M. NICULESCU^c, I. ANTONIAC^a

^aFaculty of Materials Science and Engineering, University Politehnica of Bucharest, Street Splaiul Independentei no.313, sector 6, Bucharest, Romania

^bFaculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, Street Gh. Polizu no.1-7, sector 1, Bucharest, Romania

^cDepartment of Orthopaedics and Trauma I, Colentina Clinical Hospital, Street Stefan cel Mare no.19-21, sector 2, Bucharest, Romania

The ability to adjust degradation rate of magnesium alloys is critical for the successful development of new biodegradable trauma implants. The aim of this study was to evaluate the biodegradability of an Mg0.8Ca alloy in different simulated biological medium by immersion tests and corrosion resistance testing using electrochemical measurements. The degradation of the experimental magnesium alloy was investigated by immersion tests in two different simulated medium (Simulated Body Fluid-SBF and Dulbecco's Modified Eagle Medium-DMEM) for 3, 5, 7 and 10 days at 37°C. The evaluation of corrosion resistance was performed using electrochemical measurements in the same simulated mediums for 1 hour, at 37°C. The surface morphology of the experimental sample after both tests was investigated using scanning electron microscopy - SEM. The experimental results showed that the experimental magnesium alloy Mg0.8Ca appear to be a promising biomaterial for biodegradable trauma implants but their biodegradation rate must be improved using different techniques like coatings.

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1. Introduction

Biodegradable trauma implants are becoming more and more attractive for orthopedic applications. They have a matching degradation rate and tissue healing rate, without the need for new surgery to remove the implant [1,2]. Due to several properties that make them very promising candidates to be used as degradable biomaterials for medical applications, magnesium and its alloys have been investigated very thoroughly in recent years [3].

Magnesium (Mg) and its alloys have demonstrated good biocompatibility and mechanical properties suitable to be used as trauma implants for bone fixation in orthopedic surgery [4]. Certain compositions of magnesium alloys offer appropriate mechanical properties and corrosion rates, but unfortunately, most often, the composition contains aluminum (which is neurotoxic) or rare earth elements (which are hepatotoxicity). According to the toxicological criteria, it is very important to develop new biodegradable magnesium alloys that do not contain toxic elements, but with good mechanical strength and corrosion resistance [5,6]. However, the use of these non-toxic biodegradable magnesium alloys is limited due to high corrosion and degradation rates, before the proper healing of the new tissue take place [7].

Another consequence of the corrosion process in magnesium alloys is the release of hydrogen gas (fig. 1). The rapid formation of hydrogen gas resulting from the environment that contain chlorine produces subcutaneous

gas bubbles, which generally appear within the first week after surgery and then disappear after 2 to 3 weeks. In 2007, Song postulated that a hydrogen evolution rate of 0.01 ml/cm²/day can be tolerated by the human body and does not constitute a serious threat [2]. The possibility to keep the hydrogen evolution rate below this value is given by the regulation of the corrosion rate.

Calcium (Ca) is a nontoxic element for the human body and the simultaneous release of the Mg and Ca ions is highly beneficial for the regeneration of bone tissue. This is the major reasons for the researches performed for developing magnesium alloys from the binary system Mg-Ca [4,6,8,9].

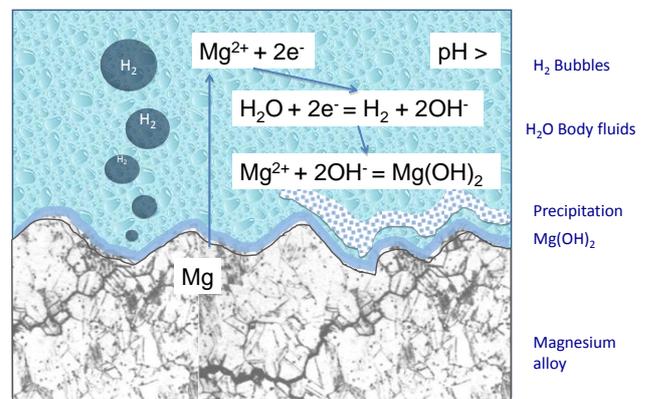


Fig.1. Schematic representation of the corrosion process in magnesium alloys.

The aim of this study was to evaluate the biodegradability of a Mg-Ca alloy in different simulated biological medium by immersion tests and corrosion resistance testing using electrochemical measurements.

2. Materials and methods

The magnesium alloy was prepared by melting 99.7% pure magnesium and calcium granules (99.8%) in an electrical resistance furnace under the protection of argon gas in a mild steel crucible. Pure magnesium has been preheated to 150 °C and then melted at a temperature of 680 °C in a sulfur dioxide atmosphere. Calcium granules were added in the melt at 680 °C after mixing, and the load was cast when it reached 620 °C. After stabilizing, molten metal with a content of 0.8 Ca wt. % was poured into mild steel mould which had been preheated at 400 °C accompanied with 30 s stirring process. After solidification and cooling in the air, the ingots were deburred and cleaned. Thus it was obtained the experimental alloy of the system Mg-Ca, respectively Mg0.8Ca. Specimens of 12x12x2mm³ were cut from the achieved alloy ingots and the samples were then mechanically wet ground with 320–4000 silicon carbide (SiC) grit papers.

The simulated mediums used to perform the *in vitro* degradation test and electrochemical corrosion test were simulated body fluid (SBF) as proposed by Kokubo [10] and Dulbecco's Modified Eagle Medium (DMEM) purchased from Sigma Aldrich.

Corrosion evaluation by electrochemical method

The corrosion resistance was determined with the Tafel technique. This technique consists of linear polarization plotting curves involving the following steps: open circuit potential measurements (E_{OC}) for 1 hour; potentiodynamic polarization plotting curves from -250 mV at (vs OC) at + 250 mV (vs OC), with a scan rate of 1 mV / s.

The evaluation test of corrosion resistance was performed using a potentiostat / galvanostat (model PARSTAT 4000, producer Princeton Applied Research, USA) and the Tafel curves were acquired using VersaStudio v.2.4 software.

In order to determine the corrosion resistance by electrochemical method it was used a corrosion cell which comprises a saturated calomel electrode (SCE) - reference electrode, a platinum electrode - recording electrode (CE) and the working electrode (WE) which consisted from the Mg0.8Ca experimental alloy.

The samples were assembled in a holder made of Teflon, so that the surface submitted to corrosion to have an area of 1 cm². The electrochemical cell was placed during the corrosion tests performance in a Faraday cage in order to protect from interference due to the electromagnetic fields.

The tests were carried out at the human body temperature (37 ± 0.5 °C) using a bath with heating and recirculation, model CW-05G. The tests were conducted in two medium that simulate the body fluids, respectively Simulated Body Fluid - SBF and Dulbecco's Modified Eagle Medium - DMEM.

Corrosion evaluation by immersion in simulated medium

The resistance to corrosion by immersion tests, respectively by determining the weight loss was achieved by immersion of the samples in simulated medium (SBF and DMEM) and maintaining them for different periods of time into a thermostatic bath at 37 ± 1 °C. The samples were weighed prior to immersion and after their removal from the medium. Also, it was performed the removal of corrosion products using a chromic acid solution without attacking the magnesium alloy residual matrix [5].

The weight loss was calculated with the following formula:

$$P.M.= ((m_0-m_t)/m_0) \times 100 \quad (1.1)$$

where: m_0 – mass of the sample before immersion; m_t – mass of the sample at various time intervals after removal of the corrosion products.

The corrosion rate can be determined by applying the equation 2.2.

$$CR= (8.76 \cdot 10^4 \cdot \Delta W) / (A \cdot t \cdot \rho) \quad (1.2)$$

where: CR - corrosion rate [mm/years]; ΔW - weight difference before and after immersion [g]; A - initial surface area exposed to corrosion [cm²]; t - immersion time [h]; ρ - alloy density [g/cm³].

3. Results and discussions

Determination of corrosion rate by electrochemical method

The Tafel curves corresponding to the Mg0.8Ca experimental alloy, recorded in both media (SBF and DMEM) are shown in Fig. 2.

The main corrosion parameters after Tafel extrapolation are showed in Table 1. The corrosion rate was calculated according to the ASTM G102-89 (2004), by using the following equation:

$$CR = K_i \frac{i_{corr}}{\rho} EW \quad (1.3)$$

where: CR is the corrosion rate, K_i is a constant (3.27×10^{-3}), ρ is the materials density, i_{corr} is the corrosion current density, and EW is the equivalent weight.

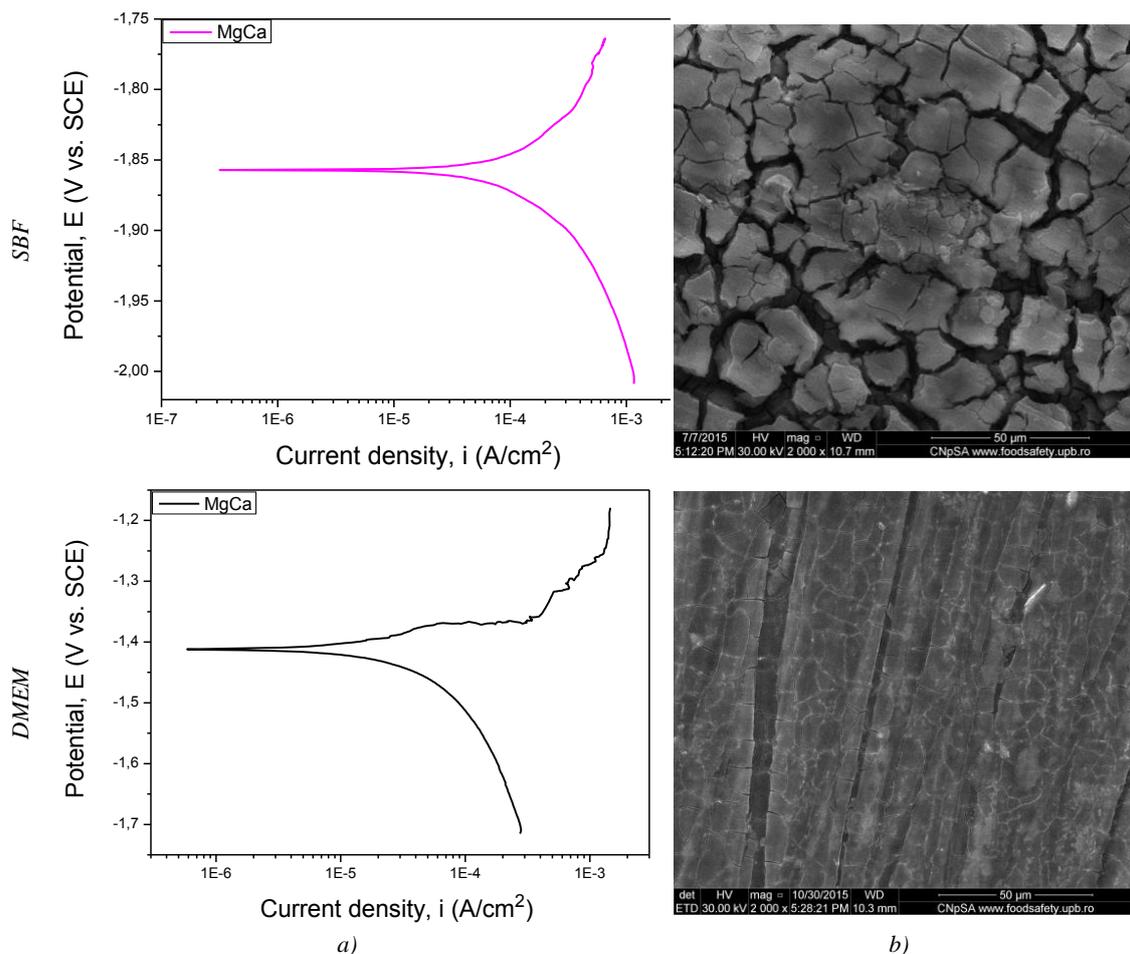


Fig. 2. Experimental results after determination of corrosion rate by electrochemical method in simulated mediums (SBF and DMEM): a) Tafel curves; b) SEM images of Mg0.8Ca alloy after corrosion test.

Corrosion resistance of Mg0.8Ca alloy has been examined from different evaluation criteria. The most electropositive corrosion potential (E_{corr}) show a better corrosion resistance. From this point of view the Mg0.8Ca alloy had a more electropositive value in DMEM used like electrolyte (-1.411 V). A lowest corrosion current density (i_{corr}) reveals a good corrosion resistance. The Mg alloy have the smallest i_{corr} with a value of $50.811 \mu\text{A}/\text{cm}^2$ in DMEM solution with a value of 10 times smaller than i_{corr} recorded in SBF solution and so, a higher corrosion resistance. Also, regarding the corrosion rate (CR) it was

observed that the Mg0.8Ca alloy had the smallest value (1.168 mm/year) in DMEM medium.

Comparing these results, it can be concluded that the Mg0.8Ca experimental alloy had a better corrosion resistance in DMEM medium.

Also, the different effect of the simulated medium on the experimental Mg0.8Ca alloy could be observed from the surface analysis performed using scanning electron microscopy. This images show a high degree of degradation with cracks all over of Mg0.8Ca alloy surface after corrosion test in SBF compared with the alloy surface after immersion in DMEM.

Table 1. The main parameters of the corrosion process of the samples in SBF and in DMEM.

Sample	E_{oc} [V]	E_{corr} [V]	i_{corr} [$\mu\text{A}/\text{cm}^2$]	R_p [$\text{k}\Omega\text{cm}^2$]	CR [mm/year]
Mg0.8Ca in SBF	-1,867	-1,857	576,046	0,14	13,247
Mg0.8Ca in DMEM	-1,498	-1,411	50,811	0,89	1,168

Determination of corrosion rate by immersion test in simulated medium

Corrosion resistance by *in vitro* degradation method was obtained by weight loss measurements which were performed by immersing the Mg0.8Ca experimental alloy samples in SBF and DMEM for 3, 5, 7, and 10 days at a temperature of 37 ± 1 °C. For testing were used four rectangular samples with dimensions of 12mm x 12mm x 2mm. Each sample was immersed in 45 ml test medium.

At the end of each period of time, samples were removed from the test medium and were cleaned in distilled water, dried in desiccators and then passed through a chromic acid solution to remove the corrosion products. After the removal of the corrosion products the samples were washed and dried. The samples were weighed initially (prior to immersion) and after removal of

corrosion products, and the corrosion rate was calculated according to the mass loss.

The corrosion rate (CR) results at various time intervals of the samples from the Mg0.8Ca experimental alloy after immersion in SBF and DMEM are shown in Fig. 3.

After immersion tests the surface morphology of the Mg0.8Ca experimental alloy was analyzed using scanning electron microscopy (fig. 4). The investigations were carried out comparative before and after removal of corrosion products. Removal of corrosion products was achieved using a solution of chromic acid and silver nitrate ($200 \text{ g L}^{-1} \text{ CrO}_3 + 10 \text{ g L}^{-1} \text{ AgNO}_3$) and led to the removal of calcium based compounds formed on the surface of Mg0.8Ca experimental samples and emphasizing corrosion occurring after the immersion test.

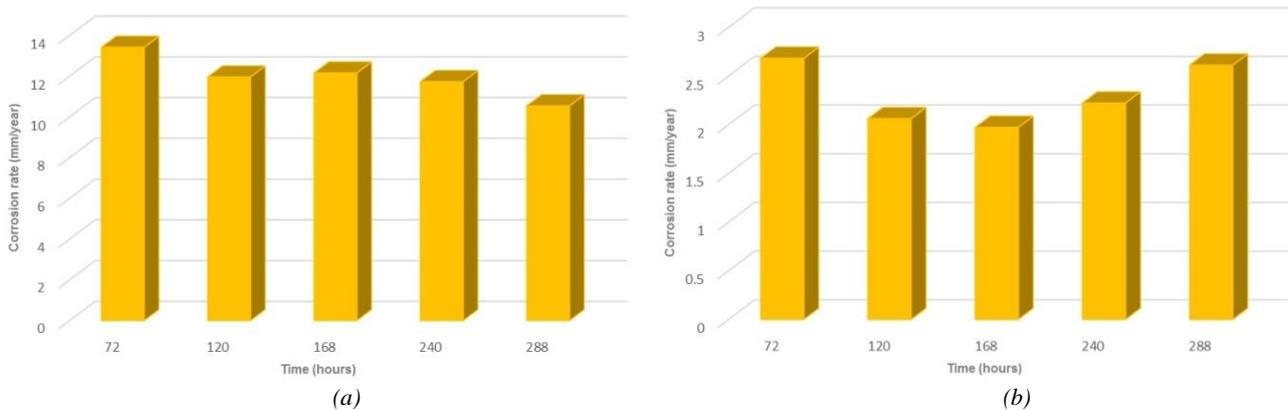


Fig.3. Corrosion rate of the experimental magnesium alloy Mg0.8Ca obtained using immersion procedure in different simulated mediums: a) SBF and b) DMEM.

Calculating the corrosion rate of Mg0.8Ca alloy at different time intervals in SBF we obtained values between $10.53 \div 13.40$ mm / year and in DMEM values between $1.97 \div 2.68$ mm / year. These values are

consistent with the values of the Mg0.8Ca alloy corrosion rate measured by electrochemical method, meaning $13,247$ mm / year in SBF and $1,168$ mm / year in DMEM (table 2).

Table 2. Corrosion rates for experimental Mg0.8Ca alloy obtained after different testing methods

Corrosion rate	Testing method	Mediums used
CR = 10,53 ÷ 13,40 mm/year	Immersion	SBF
CR = 13,247 mm/year	Electrochemical method	SBF
CR = 1,97 ÷ 2,68 mm/year	Immersion	DMEM
CR = 1,168 mm/year	Electrochemical method	DMEM

Behind testing the corrosion resistance of the Mg0.8Ca experimental alloy by immersion method, it can be seen from the SEM investigations carried out on the surface, after removing the corrosion products, a higher level of degradation when using SBF as test medium.

The surface morphology of the tested alloy in SBF is very similar to that of the crevice corrosion, presenting very deep cracks on the entire surface. When using DMEM as the test medium, the degradation rate is lower and the surface morphology is more like pitting corrosion.

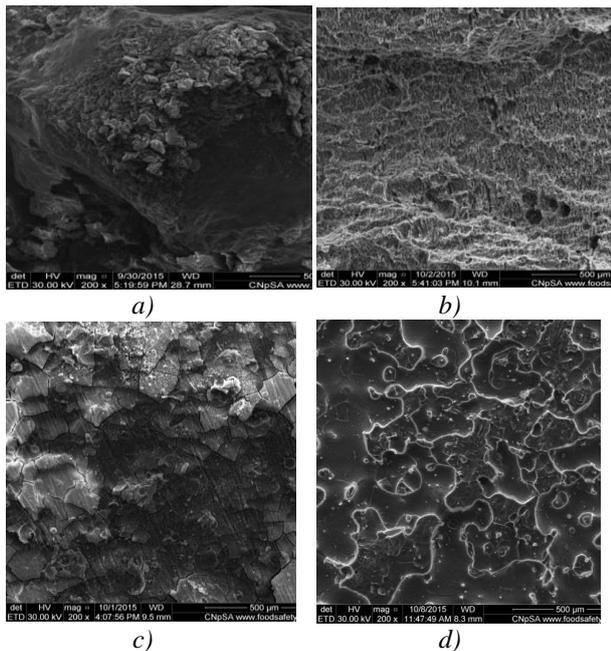


Fig.4. Comparative SEM images of the Mg0.8Ca alloy after determining the corrosion resistance in simulated mediums for 10 days using immersion procedure: a) immersion in SBF, before removing corrosion products; b) immersion in SBF, after removal of the corrosion products; c) immersion in DMEM before removing corrosion products; d) immersion in DMEM after removal of the corrosion products.

4. Conclusions

The purpose of this paper was to present a short research regarding the *in vitro* degradation and corrosion of a magnesium alloy type Mg0.8Ca. We can mention that the studied experimental magnesium alloy showed better corrosion resistance when DMEM was used as the test medium. This research add some contributions to understand the corrosion mechanism of Mg-Ca alloys by showing the influence of test medium on the biodegradation and corrosion rates and give the possibility to estimate the biodegradation rate in simulated conditions. The presented results indicate that the Mg0.8Ca magnesium alloy appear to be a promising biomaterial for biodegradable trauma implants if using a method to

control the corrosion rate, such as biodegradable ceramic coatings.

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*Corresponding author: mariusniculescu1961@gmail.com