ANNALS of Faculty Engineering Hunedoara – International Journal of Engineering
Tome XVIII [2020] | Fascicule 1 [February]

ANNALS of Faculty Engineering Hunedoara – International Journal of Engineering
ISSN 1584 - 2665 (printed version); ISSN 2601 - 2332 (online); ISSN-L 1584 - 2665

[1.]Elisa-Florina PLOPEANU, [2.]George PAPANICOLAOU, [3.]Diana PORTAN

EXPERIMENTAL RESEARCH ON THE BEHAVIOR OF BIOCOMPATIBLE MAGNESIUM ALLOYS WHEN IMMERSED IN PHYSIOLOGICAL FLUID

[1.] University "Politehnica" of Bucharest, ROMANIA
[2,3] Dept. of Mechanical Engineering & Aeronautics, University of Patras, GREECE

Abstract: The biodegradation capacity of magnesium permanently attracts the attention of the scientific researchers regarding the avoidance of the secondary surgical interventions that are required, of the removal of the implant materials after the bone healing. The various advantages of magnesium make it suitable for medical applications, being density, mechanical properties and biodegradation. The clinical applications are limited due to the accelerated corrosion of the material, as well as the alkalinity, having the effect of the release of hydrogen which causes inflammation of the adjacent tissues. Multiple application techniques on the surface of magnesium alloys for improving the biocompatibility of the surface and controlling their biocompatibility are under development. This paper presents the results of the actual experimental research about in vitro weight loss of magnesium alloys when immersed in physiological fluid.
Keywords: magnesium alloys, biomaterials, in vitro, weight loss and physiological fluid

1. INTRODUCTION

A lot of metals and alloys can be produced in the industry; however, only few are biocompatible and appropriate to be used as implant material with long-term success.

Most components for the processing of orthopaedic medical devices are materials that can be classified according to the main alloying element such as: stainless steel, cobalt-chromium alloys, titanium alloys and other types (e.g. NiTi, Mg and Ta) [1, 2].

In addition to metallic biomaterials, there are also bioresorbable polymers that can be used in orthopaedic implantology applications.

They have been the optimal solution for a long time, being used in the form of pins, bolts, plates, anchors or bows.

These polymers should show features such as the absence of block or systemic toxicity of inflammatory reactions, motorize in the totality of the human body without leaving residue after achieving the goal, easy to process and sterilize. With the spread of their use, a number of drawbacks have also been noted, such as: low mechanical strength and the occurrence of adverse local reactions of the "foreign body reaction" type, produced by the resorption of polymers and acropolymers, resulting from a enzymatic hydrolysis reaction [3].

The main concern of the present study was to determine the functionality of alloyed magnesium as biodegradable metals used in implantology.

Thus, the major component of biodegradable metals must be an essential metallic element that can be metabolized by the human body and demonstrate the rates and modes of corrosive degradation in the human body [4, 5].

Magnesium is found in the Earth's crust at a rate of approximately 2.3% of the existing metal content, with important advantages, such as low density, high intensity and stiffness, and electromagnetic shielding performance with good damping forces of the shock and vibration.

However, disadvantages would be the inability to withstand high temperatures and reduced plasticity, which limits applications [6].

Magnesium can be entirely absorbed into the human.

The merging of magnesium in chloride in environments such as the human body occurs as following [7,8].

$$Mg(s) + 2H_2O(aq) \rightarrow Mg(OH)_2(s) + H_2(g) \quad (1)$$

Magnesium reacts with water, being an abundant liquid in the human body, producing hydroxide and hydrogen. In environment with high pH (> 11.5), magnesium hydroxide will react as a barrier against corrosion, but a low pH will damage the magnesium in aqueous solution (Figure1).

The local pH at the implant-bone interface is about 7.4 or even lower, due to secondary acidosis resulting from metabolic processes and resorbable after surgical interventions, while the magnesium hydroxide layer cannot fully cover the implant surface.

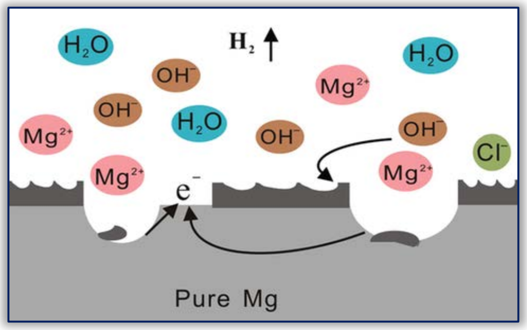

Figure 1. Schematic representation of the pure Mg corrosion

Mechanical properties of surgically implants as well as their surface properties is very important for the bio functionality of implants in various surgical specializations, orthopedy [9-11], ophthalmology [12-14] and general surgery [15,16].

Choosing the essential elements as alloying elements to optimize composition design for new biodegradable Mg alloys with good biocompatibility seems to be the most effective method of eliminating some fundamental problems.

The selection of alloying elements in biodegradable Mg alloys should be based not only on the improvement of mechanical properties, but also on the consideration of biocompatibility.

The addition of alloying elements can improve the strength of Mg by means of a grain-refining mechanism and solid solution strengthening.

Different phases in the alloys with different solid solubility provide the possibility to control the mechanical properties with different post heat treatment. The impurity elements, such as Ni, Co, Cu, and Fe, are very detrimental for the corrosion resistance of Mg alloys.

Thus, the content of such impurities needs strict limits. In addition, except for the individual effect of alloying elements, some joint effect may occur when adding more than one kind of alloying elements into Mg. For example, the existence of Al would lower approximately one order of the content of Fe. However, the addition of Zn and/or Mn would increase the limit of Fe [2].

Previously, corrosion resistance for binary and quaternary magnesium alloys has been improved by increasing the zinc concentration [17].

To conclude, selecting alloying elements for magnesium alloys to be biodegradable must be based on their biocompatibility and mechanical properties. The corrosion products of the alloys must be non-toxic, easily absorbed and dissolved by the surrounding and excreted tissues [18].

2. EXPERIMENTAL

Based on the above observation, the present investigation aimed to the manufacturing and characterization of magnesium alloys with different concentrations, as indicated in Table 1.

Table 1. The chemical composition of the investigated magnesium alloys

Product	Zn %	Zr %	Y %	Ca %	Ag %	Fe %	Si %	Ni %	Cu %	Others each %	Mg %
ZQ63	7.2	1.3	0.20	-	1.5	0.005	0.01	0.001	0.001	0.01	balance
ZQ71	6.4	1.0	0.16	-	2.5	0.004	0.01	0.001	0.001	0.01	balance
MgCa	-	-	0.02	0.99	-	0.002	0.01	0.001	0.001	0.01	balance

The immersion tests were performed as a preliminary study of degradation properties of the manufactured alloys. Prior to in vitro weight loss tests, the samples were cut into 10 mm diameter and 5 mm height, rinsed with distilled water, degreased with anhydrous ethanol solution and dried with warm air.

The immersion tests were performed in a Ringer's solution to simulate human physiological fluids (figure 3). Three samples from each type of magnesium alloy were tested (figure 3). The containers with three samples of each type of magnesium alloy placed in the heating furnace. The heating furnace and how the test samples are placed inside it are shown in the figure 4.

Three samples from each type of magnesium alloy were tested (figure 5). Specimens were immersed for 3, 5 and 7 days at 37°C and their weights were accurately measured before and after immersion.

Figure 3. Containers with Ringer's solution to simulate human physiological fluids

Figure 4. The heating furnace and containers with three samples of each type of magnesium alloy placed in the heating furnace

Figure 5. Samples from each type of magnesium alloy before immersion

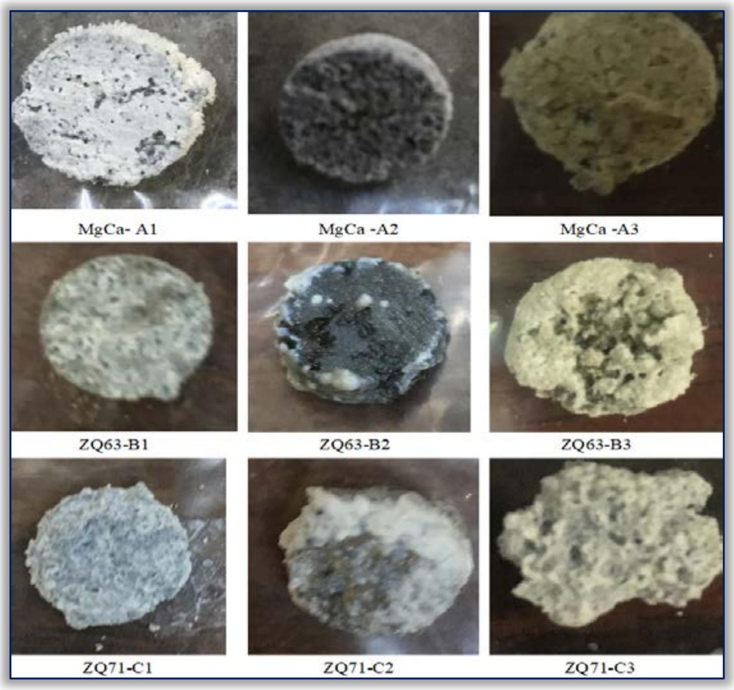

Figure 6. Samples from each type of magnesium alloy after immersion

Appearance after immersion for 3, 5 and 7 days at 37°C of the three samples from each type of magnesium alloy was tested are shown in the figure 6.

3. RESULTS AND DISCUSSIONS

The specimens were weighed before and after immersion in the saline solution and kept at a constant temperature of 28°C. On the other hand, the containers and the saline were weighed accurately, and the notations are illustrated below.

The results obtained after the immersion are presented in the tables 2-4.

Table 2. The results obtained after the immersion for MgCa magnesium alloy

MgCa=A Samples	Sample weight (g)	Containers weight (g)	Weight after degreasing (g)	Water + container weight (g)	Water + container +sample weight (g)	Weight after 3 days -wet (g)	Weight after 5 days – dry (g)	Water + container +residue weight (g)
A1	0.70	122.79	0.70	145.54	146.21	0.77	0.68	145.37
A2	0.68	124.86	0.69	143.74	144.43	0,33	0.70	143.42
A3	0.69	127.47	0.72	153.28	153.97	0.76	0.69	147.31

Table 3. The results obtained after the immersion for ZQ63 magnesium alloy

ZQ63=B Samples	Sample weight (g)	Containers weight (g)	Weight after degreasing (g)	Water + container weight (g)	Water + container +sample weight (g)	Weight after 3 days -wet (g)	Weight after 5 days – dry (g)	Water + container +residue weight (g)
B1	0.62	124.72	0.61	148.74	149.33	0.66	0.61	148.53
B2	0.54	120.86	0.55	144.38	144.93	0.65	0.54	144.24
B3	0.63	120.96	0.63	143.29	143.92	0.70	0.61	142.94

Table 4. The results obtained after the immersion for ZQ71 magnesium alloy

ZQ71=C	Sample weight (g)	Containers weight (g)	Weight after degreasing (g)	Water + container weight (g)	Water + container +sample weight (g)	Weight after 3 days -wet (g)	Weight after 5 days – dry (g)	Water + container +residue weight (g)
C1	0.61	127.23	0.61	149.75	150.37	0.53	0.50	149.74
C2	0.61	122.60	0.63	146.57	147.20	0.57	0.47	146.52
C3	0.63	118.46	0.63	143.70	144.31	0.53	0.48	146.67

4. CONCLUSIONS

By analysing the results obtained in the immersion tests in simulated body fluid of the three types of magnesium alloys studied, shown in the table 2-4, the following conclusions can be drawn:

— Of the magnesium alloys studied, the ZQ 71 alloy has the most pronounced biocompatibility character with the human body because it is assimilated most quickly in the test solution, the justification for this behaviour can be given by the presence of a higher concentration of Silver in this alloy.

— Of the ZQ63 and MgCa alloys, after the first 3 days, an increase in the weight of the samples is observed, which means that the alloy assimilates the test solution and only after 5 days of maintenance these alloys begin to decompose into the Ringer's solution.

— In all the types of magnesium alloys studied, a greater weight loss of the samples is observed at a maintenance time of 5 days in the Ringer's solution compared with the maintenance duration of 3 days, which shows a continuous assimilation in time of an alloy quantity in the Ringer's solution.

— From the studied magnesium alloys, can be made for the human body prostheses, because after a minimum of 5 days from the implant they begin to be assimilated by the bone system and no longer require further surgery to check or replace the human prosthetic implants.

Acknowledgment:

All the authors contributed equally to the development of the experimental research and were done as a result of participating of Elisa-Florina PLOPEANU in a training program at the University of Patras Greece (01/03/2018-31/05/2018).

References

[1] Maria Diana VRÂNCEANU, Iulian ANTONIAC, Rami ŞABAN, Mădălina ALBU, Development and characterization of novel porous collagen based biocomposite for bone tissue regeneration, U.P.B. Sci. Bull., Series B, Vol. 74, Iss. 3, 2012 ISSN 1454-2331, pag.145-155.
[2] D.J. Blackwood, (2003), Corros. Rev., 21, pp. 97-124.
[3] Bostman, O. M., and H. K. Pihlajamaki; (2000), Adverse tissue reactions to bioabsorbable fixation devices; Clin. Orthop., pg 216–227
[4] Florin MICULESCU, Iulian ANTONIAC, Lucian Toma CIOCAN, Marian MICULESCU, Mihai BRÂNZEI, Adrian ERNUTEANU, Dan BATALU, Andrei BERBECARU, Complex analysis on heat treated human compact bones, U.P.B. Sci. Bull., Series B, Vol. 73, Iss. 4, 2011 ISSN 1454-233, pag.203-212.
[5] Y.F. Zheng, X.N. Gu, F. Witte, (2014), Mat. Sci. Eng. R 77, pag. 1–34
[6] J. Zhang, Z.X. Guo, F.S. Pan, Z.S. Li, X.D. Luo, (2007), Effect of composition on the microstructure and mechanical properties of Mg–Zn–Al alloys, Mater. Sci. Eng. A, 456, pp. 43-51
[7] Hassel, T.; Bach, F.W.; Krause, C. Influence of alloy composition on the mechanical and electrochemical properties of binary Mg-Ca alloys and its corrosion behavior in solutions at different chloride concentrations. In Proceedings of the 7th International Conference on Magnesium Alloys and Their Applications; (2007); Kainer, K.U., Ed.; Wiley-VCH Verlag GmbH & Co.: Hoboken, NJ, USA, pp. 789–795
[8] Ana-Iulia BITA, Iulian ANTONIAC, Ion CIUCA, Potential use of Mg-Ca alloys for orthopedic applications, U.P.B. Sci. Bull., Series B, Vol. 78, Iss. 3, 2016 ISSN 1454-2331, pag. 173-183.
[9] Bita, Ana- Iulia; Stan, G.E.; Niculescu, M., et al., Adhesion evaluation of different bioceramic coatings on Mg – Ca alloys for biomedical applications, Journal of Adhesion Science and Technology, Vol. 30, Iss. 18, pages 1968 – 1983, 2016.
[10] Bita, A.I.; Antoniac, A.; Cotrut, C.; et al., In vitro degradation and corrosion evaluation of Mg- Ca alloys for biomedical applications, Journal of Optoelectronics and advanced materials, Vol. 18, Iss. 3 – 4, pages 394 – 398, 2016.
[11] Antoniac, Iulian; Negrosoiu, Mihai; Mardare, Mihai; et al., Adverse local tissue reaction after 2 revision hip replacements for ceramic liner fracture. A case report, Medicine, Vol. 96, Iss. 19, art. no. e6687, 2017.
[12] Antoniac, Iulian Vasile; Stoia, Dan Ioan; Ghiban, Brandusa; et al., Failure analysis of a humeral shaft locking compression plate surface investigation and simulation by finite element method, Materials, Vol. 12, Iss. 7, article no. 1128, 2019
[13] F Miculescu, M Miculescu, LT Ciocan, A Ernuteanu, I Antoniac, I Pencea, E Matei, Comparative studies regarding heavy elements concentration in human cortical bone, Digest Journal of Nanomaterials and Biostructures Vol. 6, No 3, July-September 2011, p. 1117-1127.
[14] M Miculescu, D Bojin, LT Ciocan, I Antoniac, Experimental researches on biomaterial-tissue interface interactions, Journal of Optoelectronics and Advanced Materials, 2007, vol 9, nr 1, pag. 3303-3306.
[15] F Miculescu, GE Stan, LT Ciocan, M Miculescu, A Berbecaru, I Antoniac, Cortical bone as resource for producing biomimetic materials for clinical use, Digest Journal of Nanomaterials and Biostructures Vol. 7, No. 4, October-December 2012, p. 1667-1677,
[16] Stefan Ioan Voicu, Roxana Mihaela Condruz, Valentina Mitran, Anisoara Cimpean, Florin Miculescu, Corina Andronescu, Marian Miculescu, Vijay Kumar Thakur, Sericin covalent immobilization onto cellulose acetate membrane for biomedical applications, ACS Sustainable Chemistry & Engineering, Vol 4, Nr 3/2016, pag.1765-1774.
[17] Pourbaix, M. Atlas of Electrochemical Equilibria in Aqueous Solutions, 2nd ed.; Natl Assn of Corrosion: Houston, TX, USA, 1974
[18] Witte, F.; Kaese, V.; Haferkamp, H.; Switzer, E.; Meyer-Lindenberg, A.; Wirth, C.J.; Windhagen, H. In vivo corrosion of four magnesium alloys and the associated bone response, (2005), Biomaterials, 26, 3557–3563
[19] Witte, F.; Kaese, V.; Haferkamp, H.; Switzer, E.; Meyer-Lindenberg, A.; Wirth, C.J.; Windhagen, H. In vivo corrosion of four magnesium alloys and the associated bone response. Biomaterials 2005, 26, 3557–3563

ANNALS of Faculty Engineering Hunedoara – International Journal of Engineering
ISSN 1584 - 2665 (printed version); ISSN 2601 - 2332 (online); ISSN-L 1584 - 2665
copyright © University POLITEHNICA Timisoara,
Faculty of Engineering Hunedoara,
5, Revolutiei, 331128, Hunedoara, ROMANIA
http://annals.fih.upt.ro