INFLUENCE OF HEAT TREATMENT ON MICROSTRUCTURE AND CORROSION BEHAVIOR OF BIODEGRADABLE Mg-Ca ALLOY

Tiberiu BIȚA[1], Iuliana CORNESCHI[2], Elena UNGUREANU[3], Ana-Iulia BIȚA[4*], Nicoleta-Daniela IGNAT[5], Horațiu DURA[6], Ioana Dana CÂRSTOC[7], Pantelie NICOLCESCU[8]

Until now, different categories of metallic materials have been studied for their use in the manufacture of implants. Magnesium and its alloys are highly desirable for the production of biodegradable implants, but they corrode too quickly in the human body, necessitating the development of a number of techniques to slow down this phenomenon.

The properly used alloying elements and subsequent heat treatments lead to microstructural changes that improve their functional properties. In the context of biodegradable materials, calcium is a special alloying addition to magnesium. Two alloys from the Mg-Ca system were used (MgCa0.8 and MgCa1.1) in order to examine the effects of heat treated structure on in some simulated body fluids.

Keywords: Mg-Ca alloys, biodegradable material, heat treatment, corrosion, microstructure

1. Introduction

For the production of implants, various kinds of metallic materials have been researched up until this point. Magnesium and its alloys are beginning to offer solutions that are of considerable interest in this field, despite the fact that titanium alloys and stainless steels are well known for their application in the field of implants [1-5]. Magnesium and its alloys combine mechanical properties and biological compatibility to have the features needed for a biodegradable implant

[1] PhD std., Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: tiberiu.bita@yahoo.com
[2] Researcher, SC ROMFIRE SRL, Bucharest, Romania, e-mail: iulicorneschi07@gmail.com
[3] Assistant, Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: elena.ungureanu1102@upb.ro
[4*] Lect., Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail : ana_iulia.blajan@upb.ro
[5] Assoc. Prof., Faculty of Entrepreneurship, Business Engineering and Management, University POLITEHNICA of Bucharest, Romania, e-mail: nicoleta_ignat@yahoo.com
[6] Prof., Faculty of Medicine, Lucian Blaga University of Sibiu, Romania, horatiudura@yahoo.com
[7] Lect., Faculty of Medicine, Lucian Blaga University of Sibiu, Romania, ioana.carstoc12@gmail.com
[8] Assoc. Prof., "Dunărea de Jos" University from Galati, Romania, nicolcescu@yahoo.com

[6]. However, magnesium corrodes prematurely in the implanted tissue [7-9], thus numerous attempts have been made to find the optimal solution for their use [10,11]. It's also possible to control how effectively biodegradable magnesium alloys resist corrosion by adjusting other alloying components as well [12]. Surface coatings, mechanical treatments, and heat treatments are among the different types of treatments that are applied. Numerous surfaces coating procedures, including fluoride coatings of Mg-Ca alloys [13-15], alkaline heat treatment [16,17], calcium phosphate coatings created by electrochemical deposition [18-20], and TiO_2 coating, have been used on magnesium alloys containing calcium. These processes have all shown improved corrosion resistance. The rate of corrosion must be taken into consideration when employing biodegradable magnesium alloys [21-26]. Some studies have used their processing employing mechanical treatments like hot rolling or equal channel angular pressing [27] for the same reason. These treatments not only control bio-corrosion but also improve mechanical qualities by refining the grain.

The purpose of heat treatments is to increase strength, which leads to greater toughness, shock resistance, hardness, and yield strength. In this study, the influence of heat treatment on the corrosion rate is assessed using two types of heat treatments (T1, T2) with various parameter values. Additionally, MgCa0.8 and MgCa1.1 magnesium calcium alloys were used in the examination of the impact of alloying component content on experimental specimens subjected to heat treatments [28, 29].

Due to its low toxicity and quick elimination from the body, magnesium has a good tolerability in the body. Different tests were conducted utilizing a variety of conditions that mimic the human environment as well as solutions that have a high chloride content in order to identify the precise constituents and the amount to which they affect the corrosion of magnesium. Regardless of the medium employed, several pertinent findings regarding the behavior to corrosion of biodegradable magnesium alloys could be made in the end [30-32]. The best possible biocompatibility, adequate mechanical capabilities, and higher resistance to corrosion are requirements when using for biodegradable implants magnesium alloys as materials, so finding suitable elements for alloying is a top priority [33]. However, some alloying elements have the potential to be toxic, which poses a serious issue when dealing with the alloying process [33-36]. Due to the importance of both Mg^{2+} and Ca^{2+} to human body, calcium is a particular alloying addition to magnesium in the context of biodegradable materials, and Mg-Ca alloys exhibit exceptional biocompatibility [37].

The presented study aims to analyze two magnesium alloys in which the calcium content varies (MgCa0.8 and MgCa1.1), after heat treatments, to observe the microstructure regarding the corrosion behavior in two simulated body fluids.

2. Experimental Methods

2.1. Materials. Development and casting of experimental alloys

The raw materials used in this study consisted of ingots made from high purity, commercially available, magnesium (99.96%) and calcium (99.8%) powder. The casting was made in an electric melting pot furnace using a Diamant type graphite crucible. Using a mixed gas protective environment of sulphur hexafluoride (SF_6), magnesium was melted and cast at 680°C to obtain alloys from the Mg-Ca system. The magnesium melt was cast into a permanent mold to produce rods with a diameter of 10 mm when calcium was added at a higher temperature, which depended on the calcium ratio in the Mg-Ca alloys.

The heat treatments were performed in a furnace that allowed the electronic programming of the heat treatment parameters (UTTIS). The temperature variation was controlled in the range ± 2 ºC. The experimental Mg-Ca alloy samples for heat treatment had the dimensions: 10 mm x 10 mm x 3 mm.

Table 1

Chemical composition for the experimental Mg-Ca alloys.

Alloy	**Ca** (wt.%)	**Mg** (wt.%)
MgCa0.8	0.8	99.2
MgCa1.1	1.1	98.9

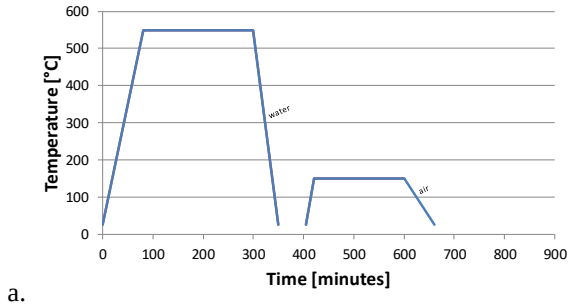
For both experimental alloys the selected heat treatment was solubilizing followed by ageing. Heating of the material is made to reach the temperature (temperature designation T1) in which the phase that initially occurs at the grain boundary is dissolved into solid solution. During rapid cooling in water this secondary phase is kept in solution, obtaining a supersaturated solid solution, out of equilibrium. The second treatment applied was ageing. This one involves the heating of the supersaturated solid solution at a suitable temperature (temperature designation T2) in order to obtain a controlled precipitation of solubilized phases in solid solution. As a result of the dispersion hardening mechanism, the mechanical characteristics are enhanced in this way. In order to achieve the desired outcomes -yield strength and hardness- the parameters -time and temperature- are selected based on the composition and other considerations.

The samples were heat-treated in a resistance furnace using a heating rate of 10˚C/min. Solubilizing quenching (T1) of the alloy was made at 550 ºC for 5h in argon atmosphere for preventing surface oxidation (which can lead to strength decrease). The cooling was done in water. Aging treatment (T2) of the solution-treated samples was made at 150˚C for different holding times: 3 h - type I and for 6 h - type II, to produce different aged microstructures and then cooled in air. The heat treatment parameters are listed in table 2.

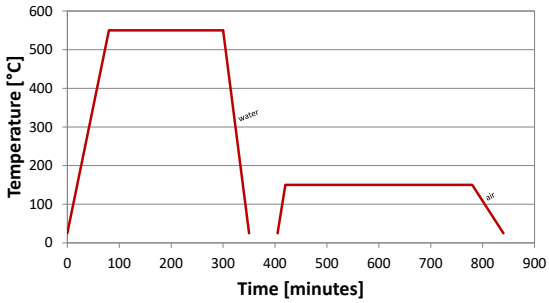
Table 2

Parameters of the heat treatments applied to the experimental Mg-Ca alloys.

Treatment	Type I	Type II
Solubilization quenching	T1: 550˚C,5h	T1: 550˚C,5h
Ageing	T2: 150˚C,3h	T2: 150˚C,6h



a.



b.

Fig. 1. Graphical representation of heat treatments applied to the experimental alloys: a. thermal regime for MgCa0.8 and b. MgCa1.1.

The equilibrium microstructure of both alloys should consist of a primary phase - α_{Mg} and a precipitated compound, Mg_2Ca, corresponding to the Mg-Ca binary diagram illustrated in Fig. 2.

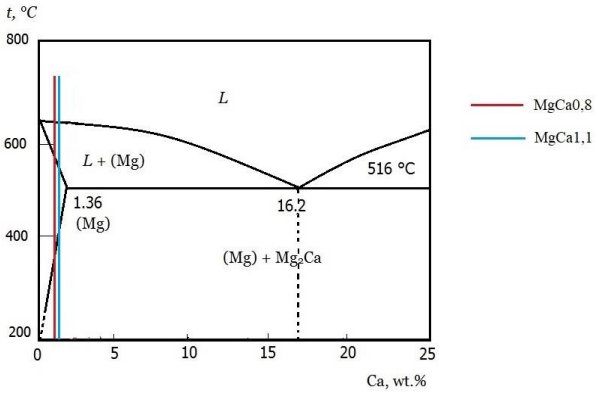


Fig. 2. Positioning of experimentally developed Mg-Ca alloys in the Mg-Ca phase diagram.

2.2. Microstructural observation

Sample preparation is an essential aspect for metallographic examination. CarbiMet^{TM} silicon carbide grinding paper in grit sizes P180 to P2000 was used for the grinding. The processes for polishing were carried out using the Buehler SumMet^{TM} kit for magnesium. Polishing of the surface of the experimental samples was made using oil-based lubricants in combination with abrasive diamond suspensions and cleaned with ethanol between polishing steps. The abrasive particles sizes were 9, 3 and 1μm, respectively. The metallographic etching was made by immersion in picric acid 3% for 2-3 s, then rinsed with ethanol and dried in cold air. Optical microscopy was used to evaluate the microstructural characteristics, using an Olympus BX51 microscope. The surface and macrostructure details of the sample were obtained with an Olympus type SZX7 stereomicroscope. Scanning electron microscope coupled with EDS for elemental composition was used for advanced microstructural features investigation.

2.3. Corrosion testing

The samples were prepared so that the usual 1 cm^2 analysis surface for corrosion behavior was achieved, according to the standard. Electrochemical examination of generalized corrosion was used to analyze corrosion behavior [38]. For the tests, an Autolab PGSTAT 128N potentiostat was employed. A corrosion cell made up of the working electrode (sample) (WE), reference electrode (RE) (Ag/AgCl), and recording electrode (CE) made of platinum was used to test the corrosion resistance using electrochemical techniques. As the electrolyte, Simulated Body Fluid and Dulbecco's Modified Eagle's Medium (SBF and DMEM) were both used at 37 ± 0.5 ℃.

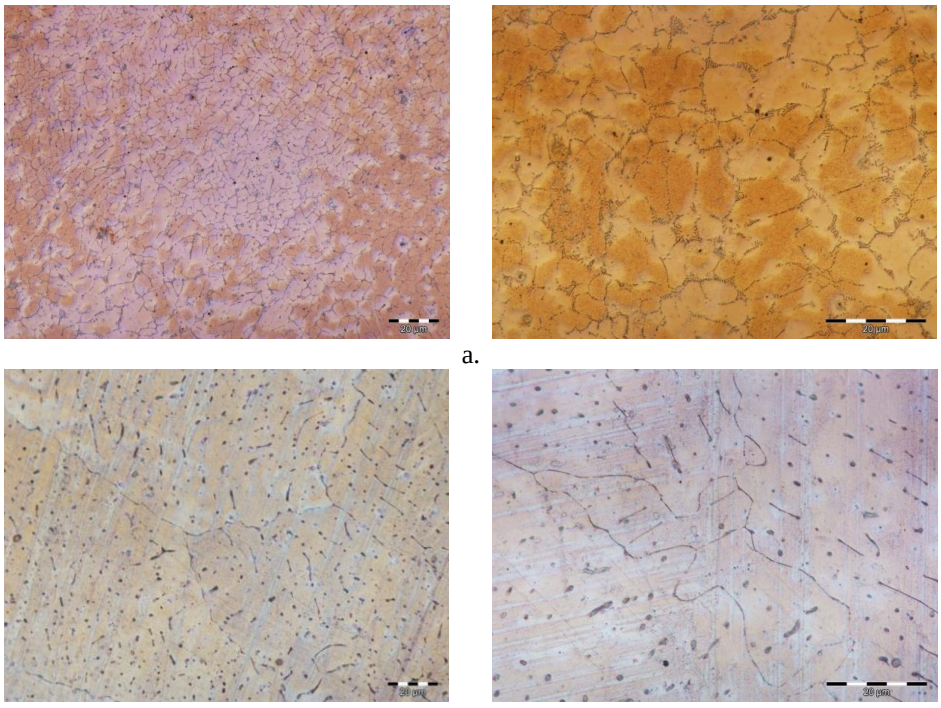
The corrosion assessment was made by recording the E_{OC} open circuit potential by immersing for 16 hours in the electrolyte. The polarization curves (Mansfeld curves) were recorded at ± 20mV vs Ag/AgCl against the E_{OC} and the polarization resistance R_p was calculated at a scanning rate of 0.4 mV/s. Further, the Tafel curves, the corrosion current (I_{corr}) and corrosion potential (E_{corr}) were obtained [38]. The calculation of the corrosion rate followed ASTM G102-89 (2004).

3. Results

3.1. Microstructure characterization

The microstructure of the analyzed magnesium alloys is presented in Fig. 3.a. and 3.b. The equilibrium structure of both alloys is formed by differently colored grains of α solid solution and precipitated secondary phases at the grain boundary of the Mg_2Ca compound. The difference between the two alloys (MgCa0.8 and MgCa1.1) consists in the fact that the second-one contains a larger amount of secondary Mg_2Ca phases, this alloy being closer to the concentration

where the solvus line starts in the equilibrium diagram. The presence of secondary phase at grains boundary induces fragility, so that both alloys, although they have an equilibrium structure, do not ensure high mechanical properties.



a.

b.

Fig. 3. Microstructure of: a. MgCa0.8 alloy before heat treatment and b. MgCa1.1 alloy before heat treatment.

Fig. 4 illustrates the microstructure of Mg-Ca alloys after heat treatment type I (Fig. 4a and 4b) and type II (Fig. 4c and 4d) respectively. The structures present grains of α solid solution and Mg_2Ca secondary phases that precipitated during aging. No major changes are observed in the structures corresponding to type I or type II heat treatments. However, a longer holding time corresponding to type II has locally determined some globulization phenomena of the precipitated secondary phases.

For MgCa1.1 alloy, after heat treatment (Fig. 4e, f, g, h) the structure seems coarser, α solid solution grains probably had a higher growth tendency during solubilization. Regarding the structural difference obtained after the application of aging (type I and II heat treatments), this is manifested by a higher density of secondary phase particles (Mg_2Ca) which precipitated as the holding time was longer. The phenomenon is considered normal, if the chemical composition of the alloy is taken into account. It has a larger amount of secondary phase in its structure, which required a longer holding time to precipitate in a controlled way during aging. The effects on mechanical properties are more

beneficial because the phenomena of precipitation hardening took place with higher intensity.

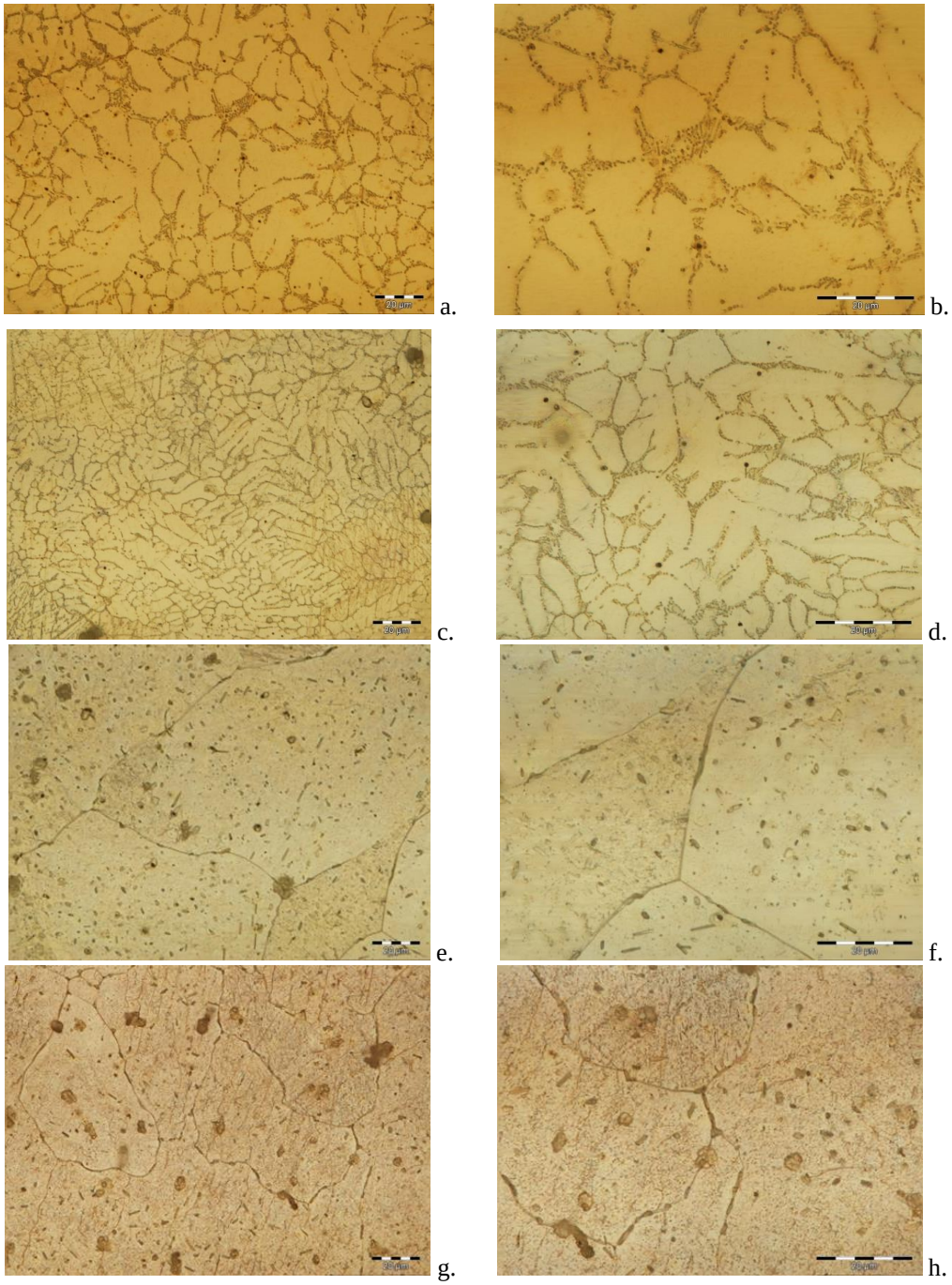


Fig. 4. Microstructure of: MgCa0.8 alloy after heat treatment type I (a. and b.) and type II (c. and d.); MgCa1.1 alloy after heat treatment type I (e. and f.) and type II (g. and h.).

Fig. 5 and Fig. 6 illustrate the scanning electron micrographs of the MgCa0.8 and MgCa1.1 alloys respectively.

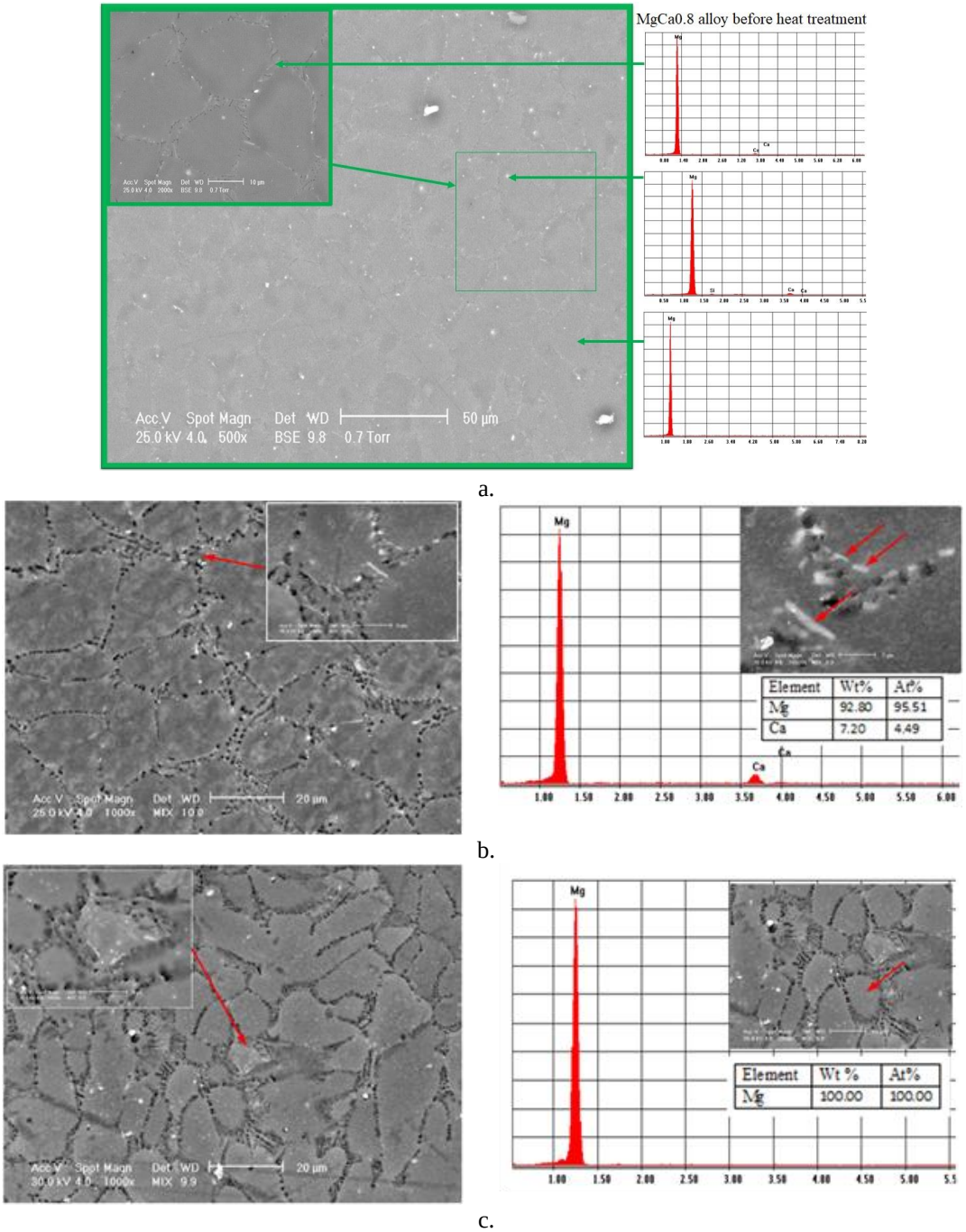


Fig. 5. Scanning electron micrographs of MgCa0.8 alloy before heat treatments (a), after heat treatment type I (b) and after heat treatment type II (c).

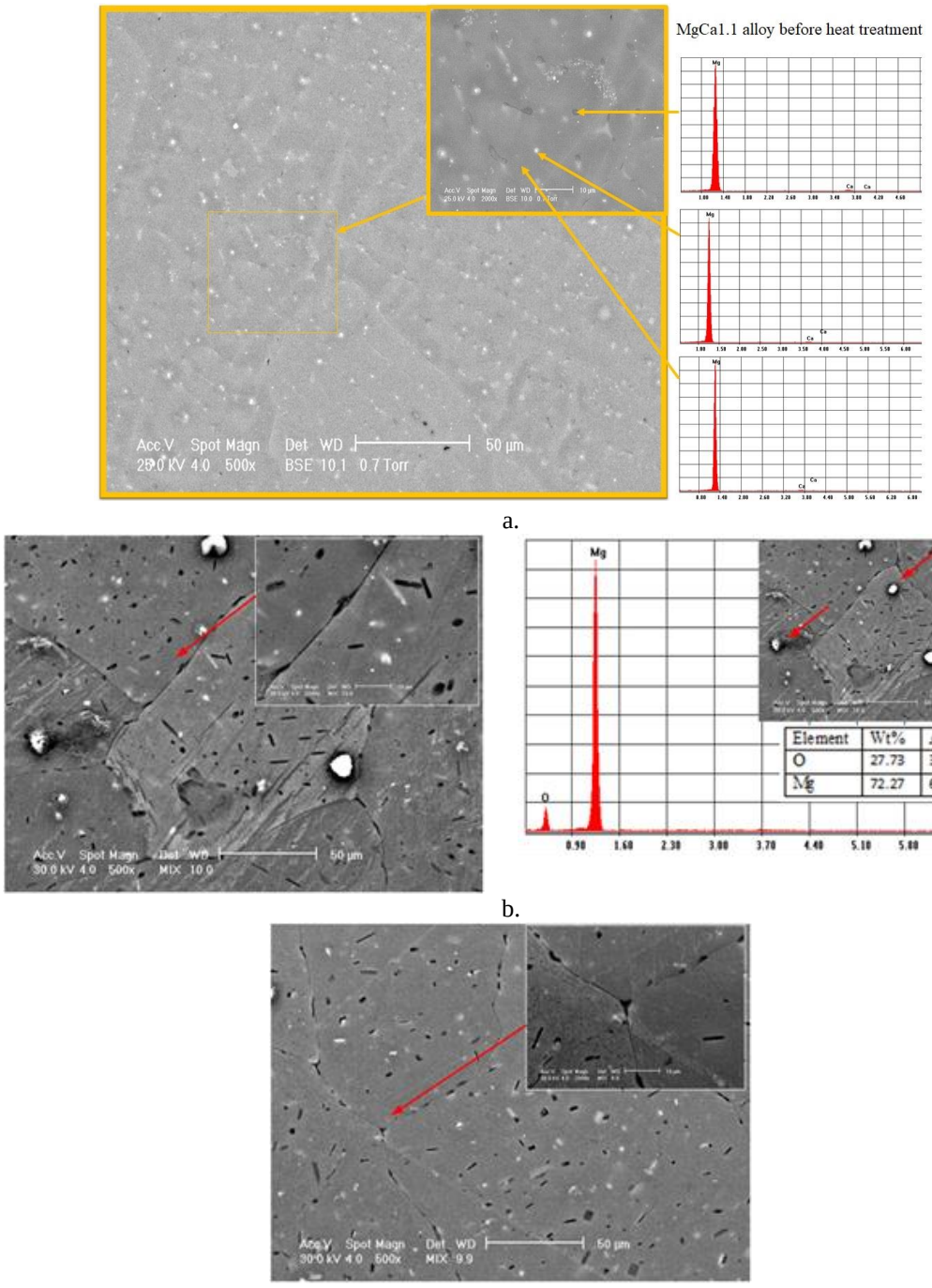


Fig. 6. Scanning electron micrographs of MgCa1.1 alloy before heat treatments (a), after heat treatment type I (b) and after heat treatment type II (c).

In the case of the untreated samples, it can be seen that the secondary phase which like a white network at the grain boundary or lamellar appearance (Fig. 5a), short bar and tiny dot shapes (Fig. 6a).

After the heat treatment the Mg_2Ca phase dissolved and precipitated into the matrix. The distribution of calcium in treated samples was found to be more homogeneous than that in the cast alloy. The surface morphology of the experimental samples subjected to heat treatments was studied using SEM, and one notable finding was the formation of cracks when the second type of heat treatment was applied to both Mg-Ca alloys. From the microstructural point of view, it could be concluded that the application of selected heat treatments has beneficial effects on the finishing of the microstructure of MgCa0.8 and MgCa1.1 alloys. However, the experimental research highlighted that the application of a heating temperature higher than 550 ºC can have negative effects on the surface of the experimental MgCa0.8 alloy.

3.2. Corrosion resistance determination by electrochemical methods

Table 3 summarizes the essential parameters of the corrosion process for the samples in SBF and in DMEM.

Tabel 3

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

Sample	E_{oc} [V]	E_{corr} [V]	i_{corr} [µA/cm^2]	Rp [Ω]	Corrosion rate [mg/m^2/day]
MgCa0,8 heat treated alloy (in SBF)	-1,591	-1,584	2,99	474,2	79,2
MgCa1.1 heat treated alloy (in SBF)	-1,556	-1,549	6,98	710,8	186,0
MgCa0.8 heat treated alloy (in DMEM)	-1,478	-1,476	0,81	4304,5	21,4
MgCa1.1 heat treated alloy (in DMEM)	-1,526	-1,521	1,12	4410,9	29,60

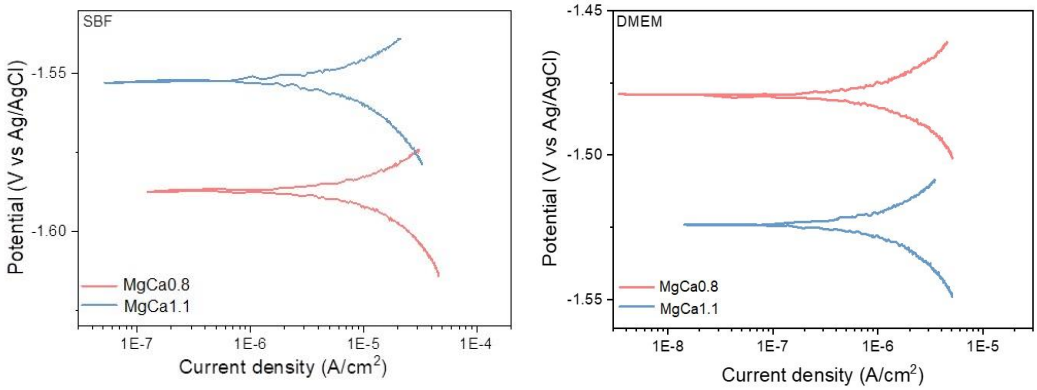
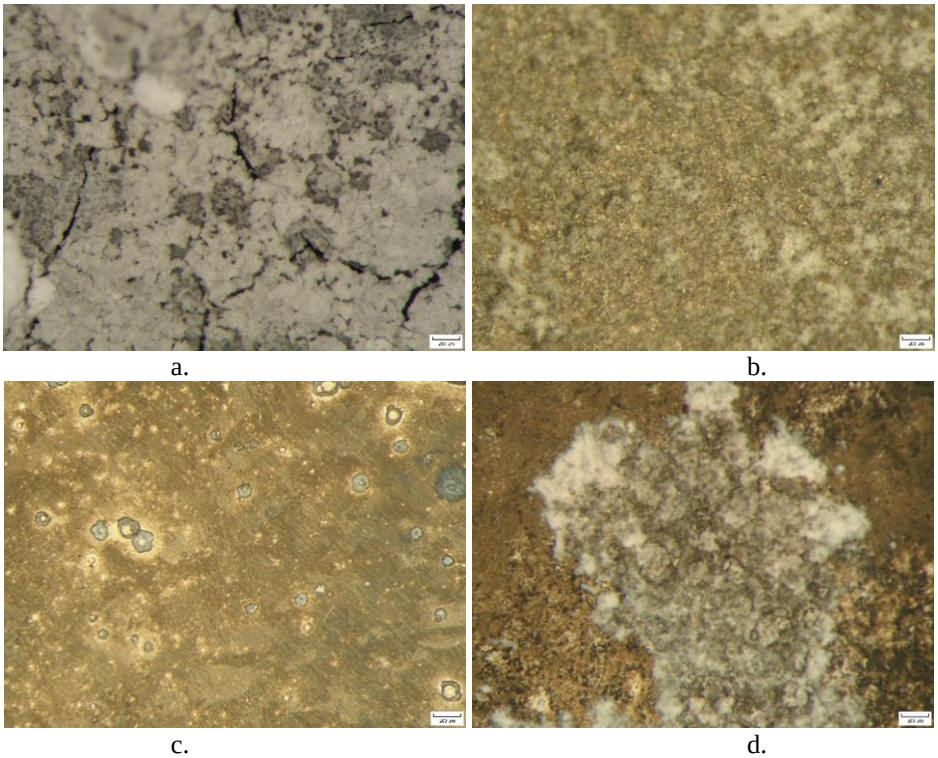


Fig. 7. Tafel curves in SBF (a) and in DMEM (b) showing the experimental results following electrochemical assessment of corrosion rate.

By contrasting the polarization curves produced for the alloys immersed in SBF, it can be seen that the alloy MgCa0.8, which has the highest electropositive value of the corrosion potential (E_{corr}), is the most corrosion-resistant. Using the same comparison criterion, it is observed in the case of immersion in DMEM that also MgCa0.8 alloy has the most electropositive value of E_{corr}.

According to the current intensities, it can be observed that by immersion in both SBF and DMEM the MgCa0.8 alloy has better corrosion resistance. Comparing the different corrosion rates obtained for different testing medium, respectively SBF and DMEM, it can be mentioned that SBF is not so aggressive medium due to the absence of proteins in his composition. DMEM is more appropriate to the human body medium [39].



a. b. c. d.

Fig. 8. Stereomicroscopy images after corrosion test in SBF of MgCa0.8 heat treated alloy (a) and of MgCa1.1 heat treated alloy (b) and in DMEM MgCa0.8 heat treated alloy (c) and of MgCa1.1 heat treated alloy (d).

4. Conclusions

It was found that both heat treatments used on the Mg0.8Ca alloy improved the grain size to be uniform. The precipitated particles are more evenly distributed contributing to the increase of mechanical performances by dispersion hardening mechanism.

According to the results obtained by microscopical techniques, it was observed that the change in the morphology of the phase (Mg_2Ca) was present at the grain boundary after heat treatments. In the sense that the Mg_2Ca phase dissolves and is distributed in the Mg matrix. Also, the distribution of calcium in treated samples was found to be more homogeneous than that in the cast alloy.

The Mg_2Ca phase uniformly precipitated by solubilization and ageing should not be in large quantities because the increase in hardness is accompanied by internal tension acting in the elastic domain. In this situation, the corrosion resistance decreases. The decrease in corrosion resistance is explained by the creation of alternating anodic and cathodic zones resulting from precipitation hardening. They act like galvanic micropyles priming the corrosive process. That is why analyzing the results obtained from the corrosion point of view, apart of the testing medium, the MgCa0.8 alloys shown a better resistance to corrosion, especially in DMEM.

Acknowledgment:

This work was funded through the Competitiveness Operational Program 2014-2020, Action 1.1.3: Creating synergies with RDI actions of the EU's HORIZON 2020 framework program and other international RDI programs, MySMIS Code 108792. The acronym project is "UPB4H", financed through the contract: 250/11.05.2020 is gratefully acknowledged.

R E F E R E N C E S

[1] *K.L. Christman*, Biomaterials for tissue repair, Science, 363 (6425) (2019), pp. 340-341.

[2] *M. Rezaei, F. Davani, M. Alishah*, Updates in immunocompatibility of biomaterials: applications for regenerative medicine, Expert Review of Medical Devices, **Vol. 19**, May 2022, pp. 353-367.

[3] *G.I. Im*, Biomaterials in orthopaedics: the past and future with immune modulation, Biomater. Res., **24** (1) (2020), pp. 1-4.

[4] *A. Vladescu, V. Pruna, S. Kulesza, V. Braic, I. Titorencu, M. Bramowicz, A. Gozdziejewska, A. Parau, C.M. Cotrut, I. Pana, M. Dinu, M. Braic*, Influence of Ti, Zr or Nb carbide adhesion layers on the adhesion, corrosion resistance and cell proliferation of titania doped hydroxyapatite to the Ti6Al4V alloy substrate, utilizable for orthopaedic implants, Ceramics International, **Vol. 45**, Issue 2, Part A, 2019, pp. 1710-1723.

[5] *Y. Zaokari, A. Persaud, A. Ibrahim*, Biomaterials for adhesion in orthopedic applications: a review, Engineered Regeneration, **1** (2020), pp. 51-63.

[6] *L. Shi, S. Chen, F. Zheng, M. Liu, H. Yang, B. Zhang*, Corrosion resistance evaluation of biodegradable magnesium alloy vascular stents optimized by mechanical adapted polymer coating strategy, Colloids and Surfaces A: Physicochemical and Engineering Aspects, **Vol. 658**, 5 February 2023, https://doi.org/10.1016/j.colsurfa.2022.130664

[7] *H. Tang, F. Wang, D. Li, X. Gu, Y. Fan*, Mechanical properties, degradation behaviors and biocompatibility of micro-alloyed Mg-Sr-RE alloys for stent applications, Materials Letters, **264**, 2020, https://doi.org/10.1016/j.matlet.2019.127285.

[8] *Y.F. Zheng, N. X. Gu, F. Witte*, Biodegradable metals, Materials Science and Engineering R, 2014, 77: 1-34.

[9] *V. Kaushik, B. Nithish Kumar, S. Sakthi Kumar, M. Vignesh*, Magnesium role in additive manufacturing of biomedical implants – Challenges and opportunities, Additive Manufacturing, **Vol. 55**, July 2022.

[10] *J. Dong, T. Lin, H. Shao, H. Wang, X. Wang, K. Song, Q. Li*, Advances in degradation behavior of biomedical magnesium alloys: A review, Journal of Alloys and Compounds, **908**, 5 July 2022, https://doi.org/10.1016/j.jallcom.2022.164600.

[11] *M. He, L. Chen, M. Yin, S. Xu, Z. Liang*, Review on magnesium and magnesium-based alloys as biomaterials for bone immobilization, Journal of Materials Research and Technology, **Vol. 23**, March–April 2023, pp. 4396-4419.

[12] *Y. Yang, C. He, E. Dianyu, W. Yang, F. Qi, D. Xie, L. Shen, S. Peng, C. Shuai*, Mg bone implant: Features, developments and perspectives, Materials & Design, **Vol. 185**, 5 January 2020, https://doi.org/10.1016/j.matdes.2019.108259.

[13] *H.R. Bakhsheshi-Rad, M.H. Idris, M.R.A. Kadir, M. Daroonparvar*, Effect of fluoride treatment on corrosion behavior of Mg–Ca binary alloy for implant application, Transactions of Nonferrous Metals Society of China, **Vol. 23**, Issue 3, pp. 699-710, 2013.

[14] *Y. Zhang, Y. Liu, R. Zheng, Y. Zheng, L. Chen*, Research progress on corrosion behaviors and biocompatibility of rare-earth magnesium alloys *in vivo* and *in vitro*, Journal of Rare Earths, Available online 11 March 2023. https://doi.org/10.1016/j.jre.2023.03.005.

[15] *H. Zhou, J. Li, J. Li, Q. Ruan, W. Jin, Z. Yu, W. Li, P.K. Chu*, Calcium phosphate coating on biomedical WE43 magnesium alloy pretreated with a magnesium phosphate layer for corrosion protection, Surface and Coatings Technology. **Vol. 401**, 15 November 2020. doi.org/10.1016/j.surfcoat.2020.126248.

[16] *K.B. Yadav, R. Kumari*, Microstructure and corrosion behavior of alkaline treated Mg-1wt.%Ca alloy, Materials Today: Proceedings. **Vol. 33**, Part 8, 2020, pp. 5667-5671, https://doi.org/10.1016/j.matpr.2020.04.151.

[17] *W.Q. Zhou, D.Y. Shan, E.H. Han, W. Ke*, Structure and formation mechanism of phosphate conversion coating on die-cast AZ91D magnesium alloy, Corrosion Sci, **50** (2008), pp. 329-337.

[18] *G.S. Hikku, C. Arthi, R.B. Jeen Robert, K. Jeyasubramanian, R. Murugesan*, Calcium phosphate conversion technique: A versatile route to develop corrosion resistant hydroxyapatite coating over Mg/Mg alloys based implants, Journal of Magnesium and Alloys, **Vol. 10**, Issue 7, July 2022, pp. 1821-1845.

[19] *Y. Liu, Y. Zhang, Y.-Li Wang, Ya-Q. Tian, L.-S. Chen*, Research progress on surface protective coatings of biomedical degradable magnesium alloys, Journal of Alloys and Compounds, **Vol. 885**, 10 December 2021, doi.org/10.1016/j.jallcom.2021.161001.

[20] *F. Witte, V. Kaese, H. Haferkamp, E. Switzer, A. Meyer-Lindenberg, C.J. Wirth, H. Windhagen*, In vivo corrosion of four magnesium alloys and the associated bone response, Biomaterials, **26**, Issue 17, 2005, pp. 3557–3563.

[21] *Yi-chi Liu, De-bao Liu, Y. Zhao, Min-fang Chen*, Corrosion degradation behavior of Mg–Ca alloy with high Ca content in SBF, Transactions of Nonferrous Metals Society of China, **Vol. 25**, Issue 10, October 2015, pp. 3339-3347.

[22] *S.E. Harandi, R.K. Singh Raman*, Corrosion fatigue of a magnesium alloy under appropriate human physiological conditions for bio-implant applications, Engineering Fracture Mechanics, **Vol. 186**, December 2017, pp. 134-142.

[23] *S. Agarwal, J. Curtin, B. Duffy, S. Jaiswal*, Biodegradable magnesium alloys for orthopaedic applications: A review on corrosion, biocompatibility and surface modifications, Materials Science and Engineering: C, **Vol. 68**, pp. 948-963, 2016.

[24] *J. Kim, H. Pan*, Effects of magnesium alloy corrosion on biological response – Perspectives of metal-cell interaction, Progress in Materials Science, **Vol. 133,** March 2023, doi.org/10.1016/j.pmatsci.2022.101039.

[25] *S. Kumar, P. Katyal*, Factors affecting biocompatibility and biodegradation of magnesium based alloys, Materials Today: Proceedings, **Vol. 52**, Part 3, 2022, pp. 1092-1107.

[26] *A. Garimella, S.B. Ghosh, S. Bandyopadhyay-Ghosh*, A comprehensive study of the impact on the microstructure and corrosion behavior of magnesium alloy-based porous bone implants, Materials Today: Proceedings, Available online 17 April 2023, doi.org/10.1016/j.matpr.2023.04.027.

[27] *H. Liu, H. Huang, X. Yang, C. Li, J. Yan, J. Jiang, A. Ma*, Microstructure and mechanical property of a high-strength Mg–10Gd–6Y–1.5Zn–0.5Zr alloy prepared by multi-pass equal channel angular pressing, Journal of Magnesium and Alloys, **Vol. 5**, Issue 2, June 2017, pp. 231-237, doi.org/10.1016/j.jma.2017.05.002.

[28] *J. Wang, J. Dou, Z. Wang, C. Hu, H. Yu, C. Chen*, Research progress of biodegradable magnesium-based biomedical materials: A review, Journal of Alloys and Compounds, **Vol. 923**, 2022, doi.org/10.1016/j.jallcom.2022.166377.

[29] *H.L. Ding, P. Zhang, G.P. Cheng, S. Kamado*, Effect of Ca addition on the microstructure and creep behaviour of AZ91 Mg alloy, Materials Today: Proceedings, Available online 16 March 2023, doi.org/10.1016/j.matpr.2023.03.056.

[30] *C. Hou, F. Qi, L. Wang, L. Lu, N. Zhao, J. She, Y. Zhou, X. Ouyang*, Effects of Ca addition on the microstructure and mechanical properties of Mg–Zn–Sn–Mn alloys, Journal of Materials Research and Technology, **Vol. 25**, 2023, pp. 3884-3900.

[31] *H. Azzeddine, A. Hanna, A. Dakhouche, L. Rabahi, N. Scharnagl, M. Dopita, F. Brisset, A.-L. Helbert, T. Baudin*, Impact of rare-earth elements on the corrosion performance of binary magnesium alloys, Journal of Alloys and Compounds, **829**, 15 July 2020.

[32] *M. Deng, L. Wang, D. Snihirova, J. Bohlen, G. Kurz, S.V. Lamaka, D. Höche, M.L. Zheludkevich*, Micro-alloyed Mg-Ca: Corrosion susceptibility to heating history and a plain problem-solving approach, Journal of Magnesium and Alloys, **Vol. 11**, Issue 4, April 2023, pp. 1193-1205.

[33] *S. Walke, V.M. Kale, P.P. Patil, J.M. Giri, H. Kumar, M. Kumar, V. Arun*, Effects of alloying element on the mechanical behavior of Mg-MMCs: A review, Materials Today: Proceedings, Available online 28 February 2023, In Press, Corrected Proof, https://doi.org/10.1016/j.matpr.2023.02.211.

[34] *H. Delavar, A.J. Mostahsan, H. Ibrahim*, Corrosion and corrosion-fatigue behavior of magnesium metal matrix composites for bio-implant applications: A review, Journal of Magnesium and Alloys, **11,** Issue 4, April 2023, pp. 1125-1161.

[35] *P. Rai, A. Rai, V. Kumar, R.K. Chaturvedi, V.K. Singh*, Corrosion study of biodegradable magnesium based 1393 bioactive glass in simulated body fluid, Ceramics International, **45,** Issue 14, 2019, pp. 16893-16903.

[36] *N. Ikeo, M. Nishioka, T. Mukai*, Fabrication of biodegradable materials with high strength by grain refinement of Mg–0.3 at.% Ca alloys, Materials Letters, **223**, 2018, pp. 65-68.

[37] *Y. Zhang, X.-hui Feng, Q.-yan Huang, Y.-ju Li, Y.-sheng Yang*, Enhancing mechanical properties and degradation performance of Mg−0.8wt.%Ca alloy by directional solidification, Transactions of Nonferrous Metals Society of China, 2011, **33**, 2023, pp. 409-421.

[38] *M. Dinu, T. Hauffman, C. Cordioli, A. Vladescu, M. Braic, A. Hubin, C.M. Cotrut*, Protective performance of Zr and Cr based silico-oxynitrides used for dental applications by means of potentiodynamic polarization and odd random phase multisine electrochemical impedance spectroscopy, Corrosion Science, **Vol. 115**, 2017, pp. 118-128, ISSN 0010-938X, doi.org/10.1016/j.corsci.2016.11.018.

[39] *H. Dong, F. Lin, A. R. Boccaccini, S. Virtanen*, Corrosion behavior of biodegradable metals in two different simulated physiological solutions: Comparison of Mg, Zn and Fe, Corrosion Science, **Vol. 182**, 2021, 109278, 2021.