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Original scientific paper

AN ASSESSMENT OF CORROSIVE PERFORMANCE OF BIODEGRADABLE ZnMgTi ALLOYS

Alexandra-Tamara Șutic[1a], Gheorghe Bădărău[1b], Romeu Chelariu[1c], Ramona Cimpoeșu[1d], Ana-Maria Roman[1e], Mihai-Adrian Bernevig[1f], Nicanor Cimpoeșu[1g,*]

[1] Faculty of Materials Science and Engineering, "Gheorghe Asachi" Technical University of Iasi, 41 Dimitrie Mangeron Blvd., 700050 Iasi, Romania
[1a] alexandra-tamara.sutic@student.tuiasi.ro, 0009-0000-4525-1661
[1b] gheorghe.badarau@academic.tuiasi.ro, 0000-0003-4233-5231
[1c] romeu.chelariu@academic.tuiasi.ro, 0000-0002-5211-358X
[1d] ramona.cimpoesu@academic.tuiasi.ro, 0000-0002-5128-4491
[1e] ana-maria.roman@academic.tuiasi.ro, 0000-0001-8798-1849
[1f] mihai-adrian.bernevig@academic.tuiasi.ro, 0000-0003-2364-3589
[1g,*] nicanor.cimpoesu@academic.tuiasi.ro, 0000-0003-4373-017X

Abstract
This study explores the viability of a novel experimental alloy, composed of zinc, magnesium, and titanium, as a prospective biodegradable metallic material for medical applications. In order to determine the samples' corrosion rates, they were subjected to electro-chemical corrosion analysis by linear and cyclic potentiometric methods. The chemical analysis of the samples was performed through the use of EDX, scanning electron microscopy (SEM), with the samples being examined in Dulbecco's Phosphate-Buffered Saline (DPBS). The obtained results revealed the impact of alloying elements on the degradation behavior, accompanied by the formation of numerous corrosion compounds. Furthermore, the study yielded findings that elucidate the interplay between microstructure, chemistry, and degradation level during the alloy's interaction with physiological fluids.

***Keywords**: ZnMgTi alloys; biodegradable metallic material; corrosion; degradation.*

1. INTRODUCTION

Research on the biodegradation properties of zinc-based alloys used for temporary medical implants remains a popular topic in the scientific community.

The experimental research on ZnTi, ZnMg, and ZnMgTi alloys generally involves the use of electrochemical methods, such as potentiostat and galvanostat, to determine corrosion potential and corrosion current density [1,2]. Additionally, gravimetric methods are employed to assess mass loss and degradation rate in artificial liquid media with a composition comparable to that of human blood plasma [3,4].

The available international literature on ZnTi and ZnMgTi alloys indicates that the addition of Ti to Zn or ZnMg systems results in the formation of intermetallic phases. These phases have been observed to act as local barriers against corrosion propagation, thereby reducing the degradation rate and favoring the formation of passive layers on the material surface [5,6]. These layers can temporarily protect the material from corrosive attack, ensuring a more controlled and predictable degradation [7].

A study by Jin et al. [5] showed that adding small amounts of Mg (<0.1 wt.%) to Zn leads to the formation of the intermetallic Mg_2Zn_{11} phase. This phase acts as a microanode in the alloy structure, accelerating the galvanic corrosion mechanism and consequently increasing the degradation rate.

Zhang et al. [6] reported that adding Mg and Ti to pure Zn creates intermetallic Mg_2Zn_{11} and $TiZn_{16}$ compounds that modify the anodic and cathodic processes on the surface of the material. This influences the corrosion mechanism through the formation of galvanic microcells and increases the degradation rate.

2. EXPERIMENTAL

An experimental ZnMgTi alloy was developed in a laboratory electric furnace with an Argon controlled atmosphere. The initial chemical composition of the ZnMgTi alloy (Table 1) was as follows: Zn: 94.91 wt% (88.04 at%), Mg: 4.49 wt% (11.20 at%) and Ti: 0.60 wt% (0.76 at%), a typical composition for modified zinc alloys for biomedical applications, where the mechanical properties and corrosion resistance of zinc are desired to be improved by the addition of elements such as Mg and Ti.

Table 1. The initial chemical composition of the experimental ZnMgTi alloy.

Element	Zn		Mg		Ti	
	wt%	at%	wt%	at%	wt%	at%
comp	94.91	88.04	4.49	11.20	0.60	0.76
St. Dev. %	0.7		0.6		0.04	

The material's electrochemical corrosion resistance was evaluated in a 3-electrode cell configuration using a potentiostat [3]. The sample surface was examined post-electrochemical corrosion resistance test using scanning electron microscopy (SEM; VegaTescan LMH II, SE detector, 30 kV) and chemical EDS analysis (Bruker 6I/10 detector, automatic and mapping analysis modes).

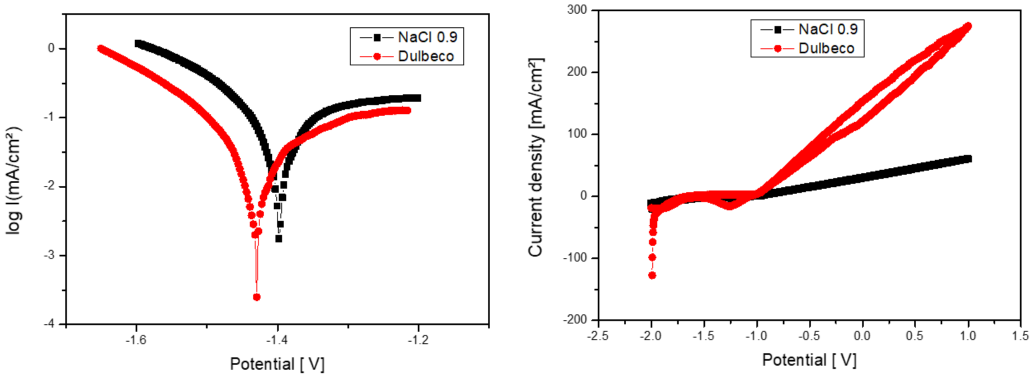
3. RESULTS AND DISCUSSION

Following the implementation of linear polarization and cyclic voltammetry tests in Dulbecco's Phosphate-Buffered Saline (DPBS), the results presented in Figure 1 indicate a substantial decrease in zinc (71.05 wt%, from 94.91 wt%), a decrease in Mg (2.56 wt%, from 4.49 wt%), an increase in Ti (2.67 wt%, from 0.60 wt%), and the emergence of new elements. The percentage values for O (18.52 wt%), Cl (2.52 wt%), and P (2.68 wt%) represent the mean values obtained from the analysis of three distinct regions on the surface, as detailed in Table 2.

Table 2. The chemical composition of ZnMgTi alloy after linear polarization and cyclic voltammetry in Dulbecco's Phosphate-Buffered Saline (DPBS).

Element / Solution	Zn		Mg		Ti		O		Cl		P	
	wt%	at%	wt%	at%	wt%	at%	wt%	at%	wt%	at%	wt%	at%
DPBS	71.05	42.4	2.56	4.12	2.67	2.17	18.52	45.16	2.52	2.78	2.68	3.38
EDS error %	1.86		0.31		0.17		3.98		0.18		0.23	

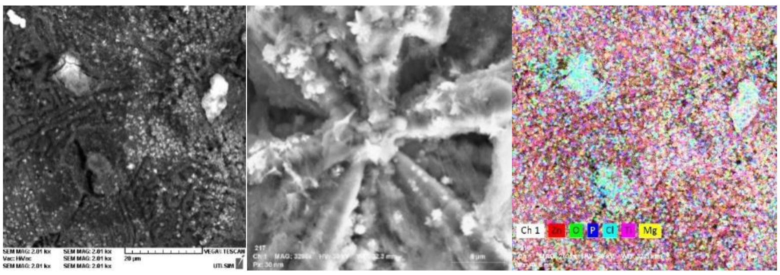
This decline in Zn and Mg content signifies a substantial corrosion of the reactive components (Zn and Mg), which dissolve in the salt solution. Zn is the primary component and the most vulnerable to anodic corrosion, particularly in media containing chloride ions (Cl-), as found in DPBS. The observed increase in Ti content is presumably attributable to the development of a passivating layer on the surface. This assertion is supported by the established stability of Ti in corrosive environments, where it has been observed to form a protective TiO_2 layer. Furthermore, elements that dissolve reduce the proportion of other more stable components. Therefore, the relative increase in Ti may also be a concentration effect. The presence of oxygen, phosphorus, and chlorine suggests the formation of oxides or hydroxides, such as ZnO, $Mg(OH)_2$, and TiO_2. P originates from phosphates in DPBS, indicating the potential for the formation of metal phosphates (e.g., Zn(PO)) and similar compounds. Cl is corrosive and promotes galvanic corrosion, leading to the formation of corrosion products in the form of metal chlorides.



(a) *(b)*

Figure 1. Electro-corrosion results of the experimental alloys (in DPBS): (a) Tafel diagrams; (b) voltammograms with cyclic curves.

The ZnMgTi alloy exhibited substantial levels of corrosion in DPBS, as evidenced by notable losses of Zn and Mg. However, the presence of Ti contributes to the formation of a protective layer that can inhibit further corrosion evolution. The presence of oxide and phosphate compounds on the surface indicates a partial self-passivation mechanism, yet it is insufficient to fully impede the dissolution of reactive metals. The electrochemical corrosion process parameters for the ZnMgTi alloy in DPBS were as follows: corrosion potential (Ecorr): -1430 mV, corrosion current density (Icorr): 0.0647 mA/cm², polarization resistance (Rp): 1.47 kO-cm² and a corrosion rate (CR) of 1.492 mm/yr. A comparison of ZnMgTi with a ZnMg alloy [8] reveals that the former exhibits a more negative corrosion potential (-1430 mV), suggesting a more anodic character. However, the low Icorr and high Rp indicate a lower corrosion rate compared to ZnMg, suggesting enhanced stability in physiological environments. The corrosion rate (1.492 mm/year) was lower than those reported for ZnMg (2-4 mm/year), which indicates that the addition of Ti contributes to the formation of a passivating layer [9, 10]. From the SEM images presented in Figure 2, it can be observed that the surface shows an uneven morphology, with preferential attack zones, but also smooth regions. Superficially deposited corrosion products can be observed as dispersed aggregates or layers.



(a) *(b)* *(c)*

Figure 2. SEM images (a), (b) and EDS mapping after the electro-corrosion test in DPBS in (c).

As illustrated in Figure 2(c), the element distribution demonstrates that O is distributed extensively, thereby confirming the formation of oxides (ZnO, TiO_2). Ti is present in certain regions, potentially as either clusters or dispersed particles, suggesting a selective formation of the TiO_2 passive layer. The presence of chlorine, although not predominant, suggests the occurrence of chloride ion adsorption without significant soluble chloride formation [11,12]. As phosphorus was detected, the potential for the formation of metal phosphates (e.g., $Zn_3(PO_4)_2$) is suggested, which may serve a protective function.

4. CONCLUSION

The ZnMgTi alloy exhibited susceptibility to corrosion in physiological environments (DPBS). However, the presence of Ti offered some degree of protection. The observed behavior is promising for biomedical applications, such as biodegradable implants, in a number of ways:

- The material's degradation is characterized by a controlled process, a property that is advantageous in specific applications.
- It has been demonstrated to be an effective method of regulating the corrosion rate.
- Corrosion products may have the potential to exhibit biocompatibility.

Incorporating Ti into the ZnMg alloy has been observed to enhance corrosion resistance by reducing Icorr and CR, and increasing Rp. This addition promotes the formation of a more stable surface, characterized by the presence of protective oxides, particularly TiO_2. This results in a more controlled distribution of corrosion products and a less aggressive morphology compared to ZnMg. These observations indicate that the ZnMgTi alloy is particularly well-suited for biomedical applications, where the controlled and uniform degradation of the material is a critical factor.

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REFERENCES

[1] X. Liu, J. Sun, Y. Yang, F. Zhou, Z. Pu, L. Li, Y. Zheng, Mater. Lett., 162 (2016) 242-5.
[2] Z. Yin, Microstructural evolution and mechanical properties of Zn-Ti alloys for biodegradable stent applications. M.S. Thesis, Michigan Technological University, 2017.
[3] A.T. Șutic, R. Chelariu, R. Cimpoeșu, A.M. Roman, B. Istrate, V. Goanță, M. Benchea, M. Moscu, A. Alexandru, N. Cimpoeşu, G. Zegan, Metals, 14 (7) (2024) 764.
[4] C. Panaghie, G. Zegan, A. Sodor, N. Cimpoeșu, N.M. Lohan, B. Istrate, A.M. Roman, N. Ioanid, Materials, 16 (2023) 3092.
[5] H. Jin, S. Zhao, R. Guillory, P.K. Bowen, Z. Yin, A. Griebel, J. Schaffer, E.J. Earley, J. Goldman, J.W. Drelich, Mater. Sci. Eng C., 84 (2018) 67-79.
[6] S. Zhang, P. Yuan, X. Wang, T. Wang, L. Zhao, C. Cui, Materials, 15 (3) (2022) 940.
[7] C. Ji, A. Ma, J. Jiang, D. Song, H. Liu, S. Guo, J. Alloys Compd., (2024) 174669.
[8] C. Panaghie, R. Cimpoeșu, G. Zegan, A.M. Roman, M.C. Ivanescu, A.A. Aelenei, M. Benchea, N. Cimpoeșu, N. Ioanid, Appl. Sci., 12 (2022) 2727.
[9] P.K. Bowen, J. Drelich, J. Goldman, Adv. Mater. Commun., 25 (18) (2013) 2577-2582.
[10] C. Ji, A. Ma, J. Jiang, D. Song, H. Liu, S. Guo, J. Alloys Compd., 993 (2024) 174669.
[11] A.T. Șutic, R. Chelariu, R. Cimpoeșu, M. Axinte, A.-M. Roman, G. Bădărău, N. Cimpoeșu, Biodegradable materials based on Zn-Mg-Ti in medicine: a promising solution for sustainable medical applications, Bulletin of the Polytechnic Institute of Iaşi, published by "Gheorghe Asachi" Technical University of Iaşi, Section Materials Science and Engineering, 70 (74) (2024) p. 31.
[12] C. Panaghie, R. Cimpoeșu, B. Istrate, N. Cimpoeșu, M.A. Bernevig, G. Zegan, A.M. Roman, R. Chelariu, A. Sodor, Materials, 14(10) (2021) 2505.