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EFFECT OF TIN (SN) ADDITION ON THE CORROSION BEHAVIOR OF HYDROXYAPATITE (HAP) COATED Mg/MgSn ALLOYS USING DIFFERENT COATING METHODS

This study investigates the effect of tin (Sn) addition on the corrosion behavior of hydroxyapatite (HAP) coated Magnesium (Mg) /MgSn alloys by using two different coating methods. Mg/Mg alloys have gained significant attention in recent years due to their lightweight, high strength, and potential for use in a wide range of industrial applications. However, their corrosion properties during cathodic reactions with abundant hydrogen evolution have limited their widespread use, particularly in biomedical applications. In this study, pure Mg, Mg2Sn, Mg3Sn, Mg4Sn, and Mg5Sn alloys were prepared by powder metallurgy method. Then samples were coated by two different methods, dip-coating and electro-deposition. Potentiodynamic polarization and hydrogen evolution reaction analysis were performed to evaluate the corrosion rate and the hydrogen volume released from the alloys. The results indicate that the addition of Sn does not significantly increase the corrosion resistance of MgSn alloys. However, the current density and hydrogen evolution of the alloys are apparently improved after the coating process. The better corrosion resistance was observed for the Mg with higher composition, which are Mg4Sn and Mg5Sn. Overall, the study demonstrates that coating HAP onto the surface of MgSn alloys is able to improve their corrosion behavior and suppress the hydrogen evolution rate (HER) of the MgSn alloys. This improvement in other ways will increase their potential for industrial applications specifically in biomedical applications.

Keywords: Magnesium alloy; Magnesium corrosion; Hydrogen Evolution Reaction; Potentiodynamic Polarization

1. Introduction

Mg-based alloys have shown great promise as biodegradable materials for biomedical applications due to their outstanding properties, biocompatibility, and potential for reducing long-term implant-related complications. The unique combination of high strength, low density, and biodegradability has positioned Mg and its alloys as viable alternatives to conventional permanent metallic implants, particularly in orthopedic and cardiovascular applications [1,2]. However, the widespread clinical implementation of Mg-based implants still faces significant challenges related to their rapid corrosion and subsequent hydrogen evolution, especially in physiological environments.

One approach to address the limitations of pure Mg is through alloying with suitable elements, which offers opportunities for tailoring the alloy's properties to meet specific application requirements. Among the alloying elements explored, Sn has garnered significant attention for its potential to enhance the corrosion resistance, biocompatibility and mechanical properties of Mg alloys. Sn with a solubility limit in Mg exceeding 5 wt.%, may significantly influence the microstructure and thereby modify the corrosion behavior of Mg-based alloys [3-7].

The incorporation of Sn into MgSn alloy is anticipated to lead to the formation of intermetallic compounds, precipitates, and grain boundary segregation, each of which can influence the corrosion kinetics and hydrogen evolution behavior. In fact, the addition of Sn in MgSn alloys can significantly influence the coating process of HAP onto the MgSn alloy surface [8-10]. It is well-known that HAP [$Ca_{10}(PO_4)_6(OH)_2$] is a bioactive ceramic material that is widely used for its excellent biocompatibility and osteoconductive properties. Other than that, $Ca_3(PO_4)_2$ coatings used in metal implantations have shown an enhancement in the biocompatibility of the implant by enhancing bone growth within the part of implanted. When coating HAP onto the MgSn alloys, the presence of Sn modifies the reactivity of the alloy, leading to the generation of specific surface sites that promote nucleation and deposition of HAP particles. This may consequently promote a uniform and dense coating. One of the notable studies claimed

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that the corrosion products of HAP and magnesium hydroxide ($Mg(OH)_2$) can completely cover the pits in the investigation of porous Mg5Sn-(HA+TCP) composites, increasing the corrosion resistance over Mg-5Sn alloy [11-12].

Moreover, the addition of Sn to the MgSn alloy may also amend the crystallographic orientation of the HAP layer. Sn can interact with the HAP crystals during the coating process, leading to changes in the preferred crystallographic orientation of the HAP coating. These modifications may affect the mechanical properties and long-term stability of the coated layer. These systems could be a promising alternative for designing and developing new provisional implants for the human body [13-16].

Recently, most of the studies have been performed focusing on only one approach, which is either focused on alloying the Mg or surface modification. In this research, we developed a new Mg alloy followed by making use of simple coating processes, which is certainly capable of reducing corrosion and promoting the growth of new bone tissue. Two different coating methods have been applied on MgSn alloys to assess the better surface modification method for biomedical applications and the corrosion behavior of HAP-coated Mg/MgSn alloys was evaluated by potentiodynamic polarization and hydrogen evaluation methods.

2. Materials & experiment

2.1. Powder metallurgy

Mg powder used in this study has a purity of 99.5%. The Sn powder used is obtained from Sigma Aldrich with a purity rate of 99%. Four different MgSn alloys were produced in this research. The alloys are designed to contain 2 wt.%, 3 wt.%, 4 wt.%, and 5 wt.% of Sn. Prior compaction process, all the powder mixtures were rolled in order to ensure the mixture was homogeneously mixed. The rolling mill was set at 100 rpm for 10 minutes. The powder then has been compacted using a manual hand pallet press at 1500 psi. Samples then being sintered in a tube furnace at 450°C after obtaining the green body. The temperature raised by 10°C/min within 2 hours of soaking time.

2.2. Optical microscopy

The samples have been ground using silica carbide grinding paper, starting from the lowest grid of 400, 600, and 800 and the highest grid with the size of 1200. Then samples are observed under an Optical Microscope. A Metal Physics Trinocular Metallurgical metallographic microscope OPTO-EDU model A13.0202 has been used in this research.

2.3. Electrochemical tests

For uncoated samples, the three-electrode cell was used for the electrochemical test. The reference electrode used is a saturated calomel electrode (SCE). Meanwhile, the counter electrode was a platinum plate and the working electrode was the sample with a surface area of 1.110 cm^2 exposed to sodium chloride (NaCl). The samples were immersed and tested in the solution for around 7 to 10 minutes. Tafel extrapolation approach has been applied to obtain the corrosion current density (icorr, mA/cm^2) of the Mg and MgSn.

2.4. Coating procedure

There are two types of coating methods have been applied in this research, dip-coating and electrodeposition method. HAP powder has been diluted in distilled water for both of the methods and acted as the coating medium. For the dip-coating method, all the MgSn alloys were dipped for 5 minutes and then baked for 30 minutes for drying purposes. Meanwhile, for the electrodeposition method, samples were immersed by applying some value of currents for 5 minutes.

2.5. Hydrogen Evolution Reaction analysis

All the HAP-coated samples were evaluated by hydrogen evolution reaction (HER) test methods. With the application of a simple HER setup, samples were immersed in 0.1M NaCl solution. The hydrogen gas that evolved was captured in the burette and the volume of the H_2 gas was calculated by subtracting the final volume from the initial volume of NaCl solution. The same procedure has been done in our previous research studies [17].

3. Results and discussion

3.1. As-sintered Mg and MgSn with different Sn concentrations

Fig. 1 shows the sample of a) pure Mg and b-e) MgSn alloys with different concentrations of Sn (2 wt.%, 3 wt.%, 4 wt.%, and 5 wt.%). Pure Mg sample shows a uniform grain distribution of Mg. However, Mg_2Sn and Mg_3Sn start showing non-uniform grain and pit sizes within the Mg matrix. Meanwhile, for Mg_4Sn and Mg_5Sn, the presence of pits and porous structures can be clearly indicated. It is believed that the occurrence of Sn elements in Mg leads to the formation of intermetallic compounds, Sn precipitates, and grain boundary segregation within the Mg matrix. On the other hand, these Sn precipitations also seem to promote the decrease in Mg grain sizes. This may consequently affect the mechanical properties of the alloys.

Fig. 2 is the potentiodynamic polarisation graph of pure Mg and MgSn alloys in a 0.1M NaCl solution. From the graph, it can be understood that the addition of Sn as an alloying element in Mg does not significantly improve the corrosion resistance of Mg. As can be seen, the presence of Sn increases the cathodic

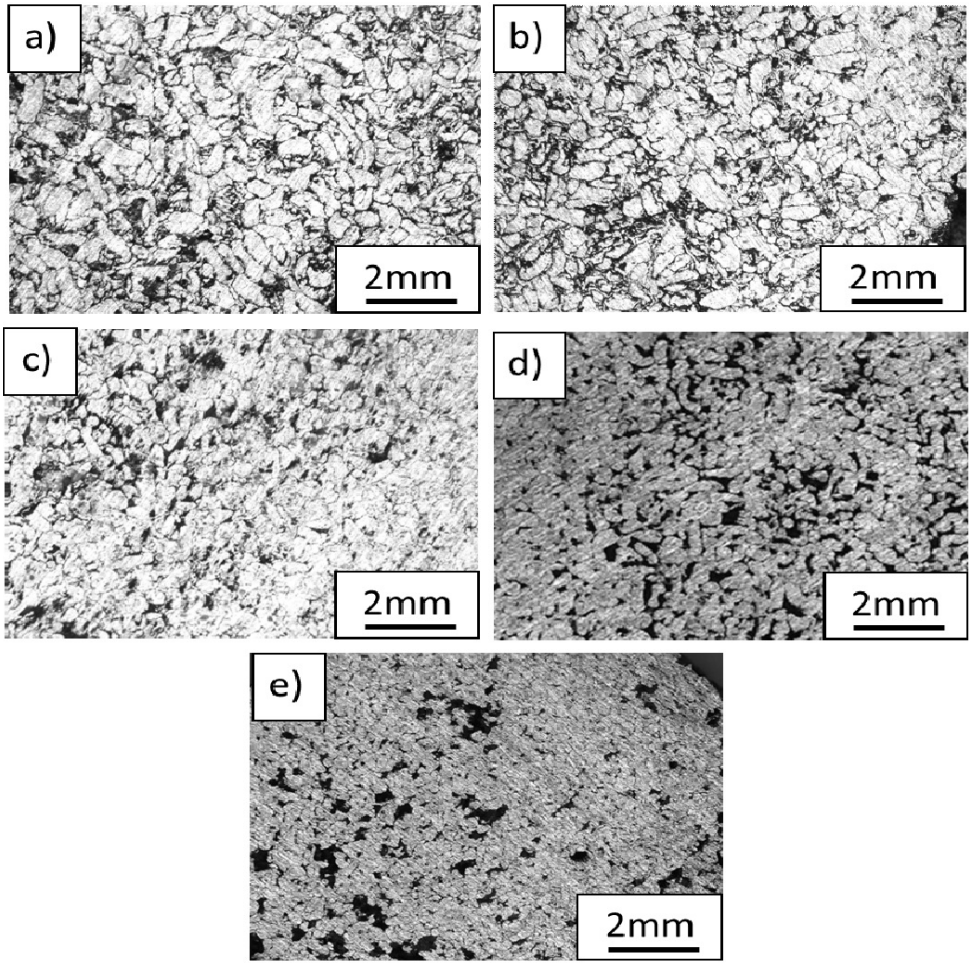


Fig. 1. Optical microscopy images of as-sintered sample a) pure Mg, b) Mg2Sn, c) Mg3Sn, d) Mg4Sn, and e) Mg5Sn

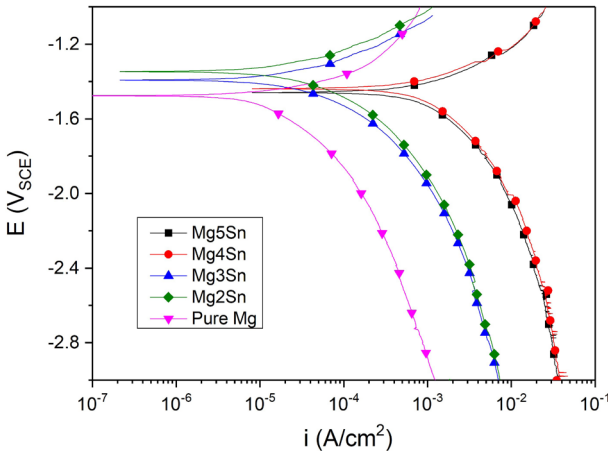


Fig. 2. Cathodic polarization of as-sintered pure Mg, Mg2Sn, Mg3Sn, Mg4Sn and Mg5Sn alloy samples in 0.1 M NaCl. Samples were polarised at a scan rate of 1 mV/s

reaction of all the MgSn alloys. The most significant current density increased in Mg with 5 wt.% of Sn.

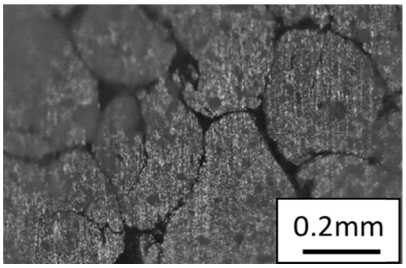
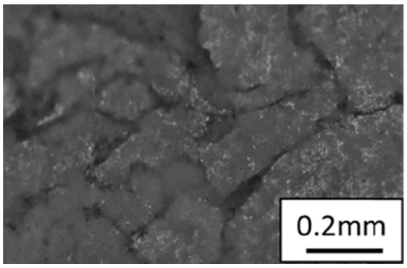
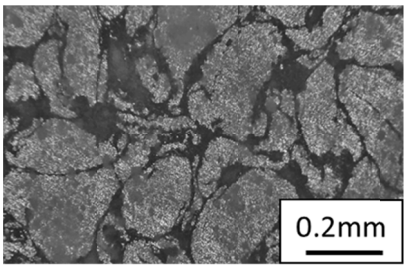
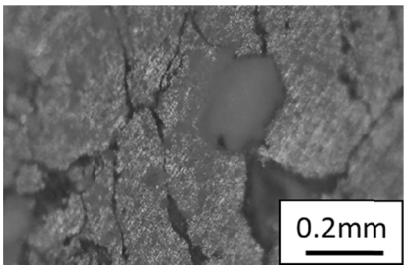
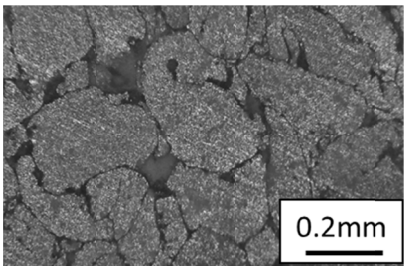
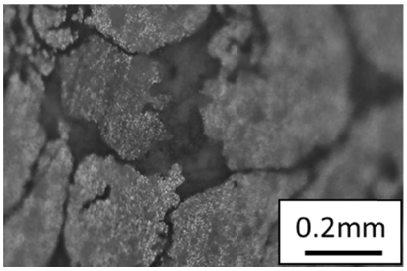
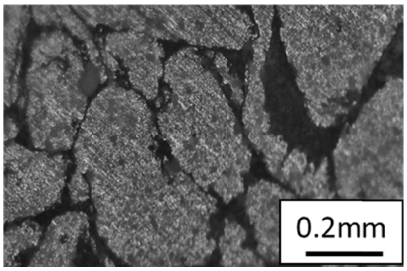
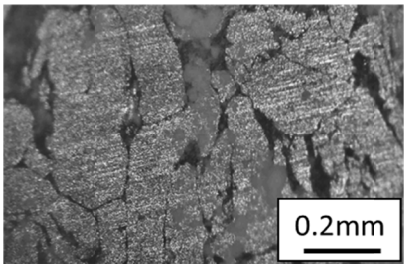
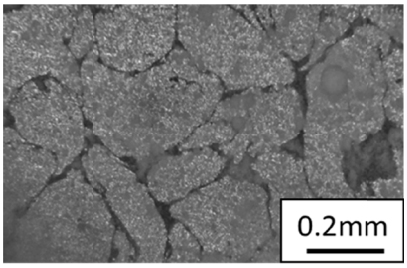
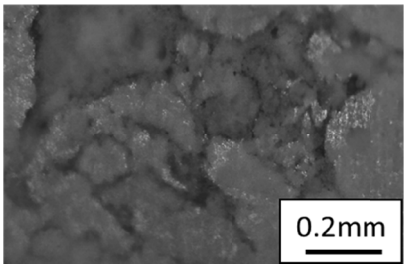
The clinical implementation of Mg-based implants is facing a significant challenge related to the hydrogen evolution reaction in physiological environments. Therefore, it is important to observe the evolution of hydrogen in the designed MgSn alloys. Fig. 3 presents the volume of hydrogen evolved from the pure Mg and MgSn alloys in 0.1M NaCl solution. All the sintered samples were immersed in the solution for 1440 minutes. The pure Mg sample is still the lowest or the most passive in the hydrogen reaction, demonstrating the same data pattern in the current density results. However, the trend of increasing the volume of hydrogen in pure Mg is still continuing even until the highest immersion time (which was 1440 min). Meanwhile, the Mg5Sn alloy is slowing down the evolution of the hydrogen, starting at 360 minutes. The rate of evolution is highest from the start of immersion as compared to other MgSn alloys.

3.2. Coated Mg and MgSn alloys

TABLE 1 presents the optical microscopic images of HAP-coated Mg and MgSn alloys. The pure Mg and MgSn alloys that had been coated by the dip-coating method showed a clear grain boundary on the surface. This is because the effectiveness of the coating method is lower as compared to the electro-deposition method. The pits and Sn precipitation can apparently be seen, and most of the area appears to be the same as the as-sintered samples. In the pure Mg sample, the coated HAP just covers the area of the Mg matrix. Meanwhile, for all the

TABLE 1

The optical microscopic images of HAP coated Mg and MgSn alloys in different coating methods

Sample	Method of Coating	
	Dip-coating	Electro-deposition
Pure Mg		
Mg2Sn		
Mg3Sn		
Mg4Sn		
Mg5Sn		

samples that have been coated by the electro-deposition method, the hazy images of HAP can be seen and are mainly distributed along the grain boundaries.

3.3. Hydrogen evolution of coated Mg and MgSn alloys

Fig. 4 and Fig. 5 show the hydrogen evolution of HAP-coated Mg and MgSn alloys (dip-coating and electrodeposition methods, respectively). The trend of both line graphs is relatively similar. However, the most interesting analysis that can be made is when the most passive hydrogen evolution occurred in the HAP-coated Mg_5Sn alloy. All the results are presented in reverse order as compared to all the uncoated hydrogen evolution data. This indicates that the presence of Sn can accelerate the formation of protective surface oxide layers, such as MgO and SnO_2. These layers act as a barrier against corrosive media. With the presence of these oxide layers, it might consequently enhance the corrosion resistance and slow down the hydrogen evolution

of MgSn alloys. On the other hand, the formation of these oxide layers is also particularly crucial for biomedical applications, where the implant's degradation rate needs to be controlled to match the tissue healing rate.

Nevertheless, for all the samples, hydrogen evolution decreased even after the dip-coating process. It can be said that by the electrodeposition method, the improvements are doubled, and the most effective coated alloy is HAP-coated Mg_5Sn. The hydrogen evolution decreases from 3.9 ml/cm^2 to 1.6 ml/cm^2.

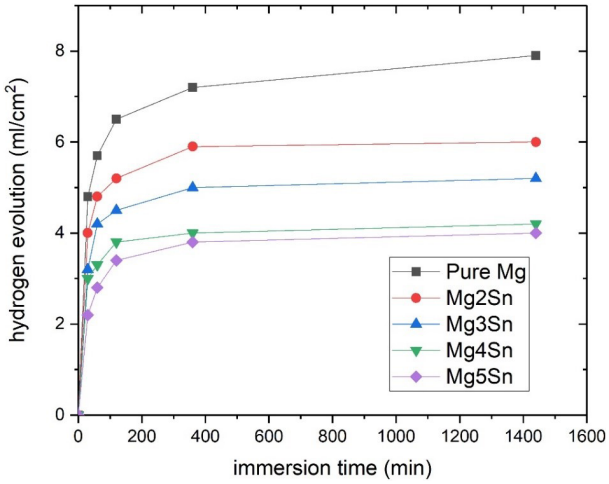


Fig. 4. The hydrogen evolution of HAP-coated Mg and MgSn alloys after dip-coating

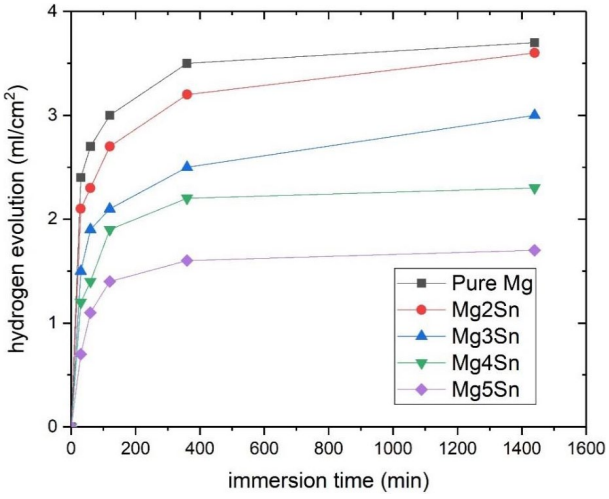


Fig. 5. The hydrogen evolution of HAP-coated Mg and MgSn alloys after electro-deposition coating

3.4. Discussion

The addition of Sn as an alloying element can significantly impact the properties and corrosion behavior of the MgSn alloy. Sn is a versatile alloying element that can modify the microstructure, mechanical properties, corrosion resistance, and biocompatibility of Mg alloys. Sn forms a solid solution structure within the Mg matrix, forming a homogeneous microstructure in the MgSn alloy. The incorporation of Sn into the Mg lattice can alter the grain size, grain boundaries, and precipitation behavior. This may also influence the mechanical properties of the MgSn alloy.

In terms of corrosion behavior, one of the main advantages of Sn addition is its ability to improve the corrosion resistance of Mg-based alloys. This also applies to the process of hydrogen evolution at the cathode area during corrosion [18-19]. This research confirmed that Sn has successfully reduced the HER by promoting a more uniform corrosion mechanism and suppressing localized hydrogen evolution. The presence of Sn may affect the formation of a protective surface oxide layer, such as MgO, $Mg(OH)_2$, and SnO_2. These types of oxide layers apparently will become a barrier against any corrosive media. On the other hand, some research done by coating CaP on Mg alloys showed that their surface morphologies changed from a plate-like structure to an agglomerated particle after 24 hours of immersion. In fact, the structure was fully covered with a newly grown apatite layer after 7 days of immersion. This compact and denser coating structure definitely provides a more uniform layer and consequently, will provide more corrosion resistance for the samples [20].

The enhanced corrosion resistance and reduced hydrogen evolution due to Sn can lead to lower levels of harmful by-products during the degradation process, making the MgSn alloy more biologically compatible. However, proper control of Sn content can tailor the degradation rate to match the tissue healing process, allowing for a temporary implant that gradually degrades as new tissue forms [21-22].

In conclusion, the addition of Sn as an alloying element can significantly impact the properties of the MgSn alloy, making it a versatile material for various engineering applications, particularly biodegradable implants and biomedical devices. The fine-tuning of the Sn content allows tailoring the alloy's properties to achieve the desired balance of mechanical strength, corrosion resistance, and biocompatibility. However, even though Sn itself is generally considered to be biocompatible, higher concentrations of Sn may have cytotoxic effects. Therefore, a vigilant balance must be designed in the Sn content to ensure optimal biocompatibility of the MgSn alloy with the HAP coating.

4. Conclusions

1. The effect of Sn on the coating of HAP on MgSn alloy plays a crucial role in determining the performance and biocompatibility of the coated implants.
2. Proper optimization of the Sn content and coating process parameters is essential to achieve a well-adhered and uniform HAP layer on the MgSn alloy, ensuring its successful application as a biodegradable implant for bone regeneration and other orthopaedic purposes.
3. Although the corrosion properties of the sintered Mg and MgSn alloys are not significantly affected, the MgSn hydrogen evolution rate has been successfully suppressed by the surface modification procedure.

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REFERENCES

[1] S. Amukarimi, M. Mozafari. Biodegradable magnesium-based biomaterials: An overview of challenges and opportunities. MedComm **2** (2), 123-144 (2021).
DOI: https://doi.org/10.1002/mco2.59

[2] A.B. Johnson, C.D. Smith, E.F. Williams, Advances in Biodegradable Magnesium Alloys for Medical Implants. Journal of Biomaterials Science: Polymer Edition **33** (15), 1801-1822 (2022).
DOI: https://doi.org/10.3390/met12091500

[3] S.V. Satya Prasad, S.B. Prasad, K. Verma, K.M. Raghvendra, V. Kumar, S. Singh, The role and significance of Magnesium in modern day research – A review. Journal of Magnesium and Alloys **10**, 1, 1-61 (2022).
DOI: https://doi.org/10.1016/j.jma.2021.05.012

[4] M. Echeverry-Rendón, L.F. Berrio, S.M. Robledo, J.A. Calderón, J.G. Castaño, F. Echeverría, Corrosion Resistance and Biological Properties of Pure Magnesium Modified by PEO in Alkaline Phosphate Solutions. Corros. Mater. Degrad. **4** (2), 196-211 (2023).
DOI: https://doi.org/10.3390/cmd4020012

[5] D.B. Panemangalore, R. Shabadi, M. Gupta, L. Lesven, Microstructure and Corrosion Behavior of Extruded Mg-Sn-Y Alloys. Metals **11**, 1095 (2021).
DOI: https://doi.org/10.3390/met11071095

[6] W. Jiang, J. Wang, W. Zhao, Q. Liu, D. Jiang, S. Guo, Effect of Sn addition on the mechanical properties and bio-corrosion behavior of cytocompatible Mg–4Zn based alloys. Journal of Magnesium and Alloys **7**, 1, 15-26 (2019).
DOI: https://doi.org/10.1016/j.jma.2019.02.002

[7] X. Chen, Y. Zhang, M. Cong, Y. Lu, X. Pi, Effect of Sn content on microstructure and tensile properties of as-cast and as-extruded Mg−8Li−3Al−(1,2,3)Sn alloys. Transactions of Nonferrous Metals Society of China **30**, 8, 2079-2089 (2020).
DOI: https://doi.org/10.1016/S1003-6326(20)65362-6

[8] X. Gu, W. Zhou, Y. Zheng, L. Dong, Y. Xi, D. Chai, Microstructure, mechanical property, bio-corrosion and cytotoxicity evaluations of Mg/HA composites. Mater. Sci. Eng. C. **30**, 827-832 (2010).
DOI: https://doi.org/10.1016/j.msec.2010.03.016

[9] Z. Zhen, T. Xi, Y. Zheng, L. Li, L. Li, In vitro study on Mg–Sn–Mn alloy as biodegradable metals. Mater. Sci. Technol. **30**. 675-685. (2014). DOI: https://doi.org/10.1016/j.jmst.2014.04.005

[10] H.-Y. Ha, J.-Y. Kang, S.G. Kim, B. Kim, S.S. Park, C.D. Yim, B.S. You. Influences of metallurgical factors on the corrosion behaviour of extruded binary Mg–Sn alloys. Corros. Sci. **82**, 369-379 (2014). DOI: https://doi.org/10.1016/j.corsci.2014.01.035

[11] P. Chander, S. Singh, I. Farina, F. Fraternali, L. Feo. Physical-mechanical characterization of biodegradable Mg-3Si-HA composites. PSU Res. Rev. **2**, 152-174 (2018).

[12] X. Wang, J.T. Li, M.Y. Xie, L.J. Qu, P. Zhang, X.L. Li. Structure, mechanical property and corrosion behaviors of (HA + β-TCP)/Mg–5Sn composite with interpenetrating networks. Mater. Sci. Eng. C. **56**, 386-392 (2015).
DOI: https://doi.org/10.1016/j.msec.2015.06.047

[13] Leonardo Hernández, Violeta Barranco, Yaymarilis Veranes Pantoja, Biomimetic hydroxyapatite (HAp) coatings on pure Mg and their physiological corrosion behavior. Ceramics International **48** (2), (2021).
DOI: https://doi.org/10.1016/j.ceramint.2021.09.206

[14] Z.-H. Zhao, Z.-M. Hua, D.W. Li, D.S. Wei, Y. Liu, J.G. Wang, D. Luo, H.Y. Wang, Effect of Sn Content on the Microstructure, Mechanical Properties and Corrosion Behavior of Biodegradable Mg–x (1, 3 and 5 wt.%) Sn–1Zn–0.5Ca Alloys. Materials **11**, 2378 (2018).
DOI: https://doi.org/10.3390/ma11122378

[15] A.M.A Mohamed, F.H. Samuel, A.M. Samuel, H.W. Doty, S. Valtierra, Influence of Tin Addition on the Microstructure and Mechanical Properties of Al-Si-Cu-Mg and Al-Si-Mg Casting Alloys. Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science **39**, 490-501 (2008).
DOI: https://doi.org/10.1007/s11661-007-9454-5

[16] Q. Zhang, Q. Li, X. Chen, The effects of Sn content on the corrosion behavior and mechanical properties of Mg–5Gd–3Y–xSn–0.5Zr alloys. RSC Adv. **11**, 1332-1342 (2021).
DOI: https://doi.org/10.1039/D0RA08986A

[17] S.H. Salleh; W.E. Jantan, R.A. Malek, S.S.C. Abdullah, P. Balan, The hydrogen evolution of pure magnesium in different electrolytes. AIP Conference Proceedings **2339**, 020238 (2021).
DOI: https://doi.org/10.1063/5.0044518

[17] L. Hou, Z. Li, H. Zhao, Y. Pan, S. Pavlinich, X. Liu, X. Li, Y. Zheng, L. Li, Microstructure, Mechanical Properties, Corrosion Behavior and Biocompatibility of As-Extruded Biodegradable Mg–3Sn–1Zn–0.5Mn Alloy. Journal of Materials Science & Technology **32**, 9, 874-882 (2016).
DOI: https://doi.org/10.1016/j.jmst.2016.07.004

[18] P. Kumar. A.K. Bhargava. Y.V. Prasad, S.S. Govind, Effect of Tin Additions on Microstructure and Mechanical Properties of Sand Casting of AZ92 Magnesium Base Alloy. Mat. Sci. Res. India **10** (2). DOI: http://dx.doi.org/10.13005/msri/100205

[19] B. Bakin, T. Koc Delice, U. Tiric, I. Birlik, F. Ak Azem, Bioactivity and corrosion properties of magnesium-substituted CaP coatings produced via electrochemical deposition. Surface and Coatings Technology **301**, 29-35 (2016).
DOI: https://doi.org/10.1016/j.surfcoat.2015.12.078

[20] J. Ma, Q. Wei, T. Le, J. Wang, P. Jin Effect of Sn addition on the microstructure and mechanical properties of AZ31 alloys. Materials Research Express **7**, 12 (2020).
DOI: https://doi.org/10.1088/2053-1591/abcda8

[21] R. Radha, D. Sreekanth, Mechanical, in vitro corrosion and bioactivity performance of Mg based composite for orthopedic implant applications: Influence of Sn and HA addition. Biomedical Engineering Advances **3**, 100033 (2022).
DOI: https://doi.org/10.1016/j.bea.2022.100033