IN-VITRO CORROSION PROPERTIES OF QUATERNARY Mg-Zn-RE-*x*Ca ALLOYS FOR BIOMEDICAL APPLICATIONS

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ABSTRACT

Magnesium (Mg) and its alloys have been intensively studied as biodegradable implant materials as they do not require secondary surgical procedure for removal compared to the traditional metallic implant materials such as stainless steels, titanium alloys and cobalt chromium alloys. Apart from that, their relatively similar mechanical properties to bone structure make them as the attractive candidates for orthopaedic applications. Nevertheless, Mg has relatively poor corrosion resistances, rapid degradation rate and hydrogen gas evolution. This phenomenon limited the usage of Mg in biomedical applications. Hence, the corrosion properties of Mg-Zn-RE-*x*Ca alloy were investigated by adding different amount of calcium (Ca). The alloys were produced using casting process and followed by immersion in Kokubo solution for 168 hours at room temperature to investigate the corrosion properties. Apart from immersion test, polarization and pH variation tests were also conducted to study the corrosion behavior of the alloys. The microstructure and morphology of the as-cast alloys were observed using optical microscope (OM). Other characterizations such as X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were used to investigate the phase formation, microstructures and elemental compositions of the as-cast and corroded specimens. Mechanical property such as hardness was investigated using Vickers hardness tester. It was found that formation of secondary IM1 ($Ca_3Mg_xZn_{15-x}$) ($4.6 \leq x \leq 12$) and Mg_2Ca phases were observed when the Ca added in the alloys. The results also showed that the addition of Ca refine the grain size thus provide higher hardness. The addition of 0.5 wt.% Ca content was found to produce the lowest dissolution rate and highest corrosion resistance. However, further addition of Ca up to 6 wt.% led to an increased in corrosion rate.

ABSTRAK

Magnesium (Mg) dan aloinya telah dikaji secara intensif sebagai bahan implan biodegradasi kerana bahan tersebut tidak memerlukan prosedur pembedahan kedua untuk penyingkiran implan berbanding dengan bahan-bahan implan tradisional yang diperbuat daripada logam seperti keluli tahan karat, aloi titanium dan aloi kromium kobalt. Selain itu, sifat mekanikal yang agak serupa dengan struktur tulang menjadikan bahan implant aloi Mg sebagai calon yang menarik untuk aplikasi ortopedik. Walau bagaimanapun, Mg mempunyai rintangan kakisan yang rendah, kadar degradasi dan evolusi gas hydrogen yang tinggi. Fenomena ini menghadkan penggunaan Mg dalam aplikasi bioperubatan. Oleh itu, sifat kakisan aloi Mg -Zn -RE - *x*Ca telah dikaji dengan penambahan unsur kalsium (Ca) yang berbeza. Proses tuangan digunakan untuk menghasilkan aloi dan seterusnya aloi-aloi tersebut direndam dalam larutan Kokubo selama 168 jam pada suhu bilik untuk mengkaji sifat kakisan. Selain daripada ujian rendaman, ujian pengutuban dan variasi nilai pH juga telah dijalankan untuk mengkaji kelakuan kakisan aloi. Mikrostruktur dan morfologi aloi telah diperhatikan dengan menggunakan mikroskop optic (OM). Pencirian lain seperti belauan sinar-X (XRD), mikroskopi electron imbasan (SEM) dan spektroskopi serakan tenaga (EDS) telah digunakan untuk mengkaji pembentukan fasa, mikrostruktur dan komposisi aloi dan spesimen yang terkakis. Selain itu, sifat mekanik seperti kekerasan telah dikaji menggunakan penguji kekerasan Vickers. Hasil kajian menunjukkan bahawa pembentukan fasa sekunder; IM1 ($Ca_3Mg_xZn_{15-x}$) ($4.6 \leq x \leq 12$) dan Mg_2Ca dapat dilihat apabila Ca ditambahkan ke dalam aloi. Hasil kajian juga menunjukkan penambahan Ca mengecilkan saiz butiran dan dengan itu menambahkan kekerasan aloi. Penambahan 0.5 % berat Ca didapati memberikan kadar keterlarutan yang terendah dan rintangan kakisan yang tertinggi. Walau bagaimanapun, penambahan Ca sehingga 6 % berat meningkatkan kadar kakisan aloi.

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LIST OF ABBREVIATIONS

Al	-	Aluminium
AP	-	Artificial Plasma
ASTM	-	American Society for Testing and Materials
BCC	-	Body-Centered Cubic
BSE	-	Backscattered Electrons
Ca	-	Calcium
Ce	-	Cerium
Co	-	Cobalt
CO_2	-	Carbon Dioxide
Cr	-	Chromium
CR	-	Corrosion Rate
DMEM	-	Dulbecco’s Modified Eagle’s Medium
Dy	-	Dysprosium
EDS	-	Energy Dispersive X-Ray Spectroscopy
Er	-	Erbium
Eu	-	Europium
Fe	-	Iron
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier transformed infrared spectroscopy
Gd	-	Gadolinium
GR	-	Grain Refiner
H_2O	-	Water
HA	-	Hydroxyapatite
HCO_3^{2-}	-	Carbonate
HCP	-	Hexagonal Close-Packed
Ho	-	Holmium
HTS	-	High Temperature Strength

KCl	-	Potassium Chloride
La	-	Lanthanum
Li	-	Lithium
Lu	-	Lutetium (Lu)
Mg	-	Magnesium
$Mg(OH)_2$	-	Magnesium Hydroxide
$MgCl_2$	-	Magnesium Chloride
MgO	-	Magnesium Oxide
Mn	-	Manganese
Mo	-	Molybdenum
NaCl	-	Sodium Chloride
Nd	-	Neodymium
Ni	-	Nickel
O_2	-	Oxygen
OM	-	Optical microscopy
P	-	Phosphorus
PDS	-	Poly P-Dioxanon
PGA	-	Polyglycolic Acid
PLA	-	Poly L-Lactic Acid
Pm	-	Promethium
PMMA	-	Poly Methyl Methacrystal
PO_4^{3-}	-	Phosphate
Pr	-	Praseodymium
RE	-	Rare earth
SBF	-	Simulated Body Fluid
Sc	-	Scandium
SCE	-	Saturated Calomel Electrode
SE	-	Secondary Electrons
SEM	-	Scanning Electron Microscopy
SiC	-	Silicon Carbide
SO_2	-	Sulfur Dioxide
Tb	-	Terbium
Ti	-	Titanium
Tm	-	Thulium

UCS	-	Ultimate Compressive Stress
UTS	-	Ultimate Tensile Stress
W	-	Tungsten
XRD	-	X-Ray Diffraction
Y	-	Yttrium
Yb	-	Ytterbium
Zn	-	Zinc
Zn	-	Zinc
Zr	-	Zirconium
Zr	-	Zirconium

LIST OF SYMBOLS

%	-	percentage
°C	-	centigrade degree
at.%	-	atomic percentage
cm^{-1}	-	per centimeter
E	-	Young's Modulus
E_{corr}	-	Corrosion potential
g/ cm^3	-	gram per centimeter cube
GPa	-	gigapascal
Hv	-	Vicker's hardness
i_{corr}	-	Corrosion current density
kg	-	kilogram
kV	-	kilovolt
mg	-	milligram
mm	-	millimeter
mm/y	-	millimeter per year
mmol/L	-	millimol per litre
MPa	-	megapascal
ms	-	millisecond
P_i	-	Corrosion rate
t	-	Average crystallite size (nm)
V	-	volt
wt. %.	-	weight percentage
β	-	Diffraction peak width at mid-height
θ	-	Bragg diffraction angle
λ	-	X-ray wave length
ρ	-	Density

CHAPTER 1

INTRODUCTION

1.1 Background

Biomaterial implants are used as a replacement of a bone part or as a support in the healing process. Replacement of a bone part requires implants to stay in the body permanently, while support only requires that the implant remain in the body for a shorter period. When permanent implant is used for a temporary application, additional surgeries are required to remove these devices after the healing process. Thus, removal process increases the patient grim and cost of health care. In contrast, biodegradable materials require no additional surgeries for removal as they dissolve after the healing process is complete. This also eliminates the complications associated with the long term presence of implants in the body. Finally, after these materials degrade within the body, it is important that the body can metabolized the degradation products, and thus are bio-absorbable (Li and Zheng, 2013).

The first materials to be used as commercial biodegradable and bioabsorbable implant materials were polymers. The most commonly and earliest used absorbable materials include polyglycolic acid (PGA), poly L-lactic acid (PLA), and poly P-dioxanon (PDS). However, applications of polymeric materials in load-bearing and tissue supporting applications is severely restricts due to low strength as the mechanical needs of the body required a greater amount of material (Brar *et al.*, 2009).

Metals due to their relatively high strength and fracture toughness possesses desirable mechanical properties, however, most of the metals are biologically toxic. Conventional implant, like cobalt, stainless, chromium, and nickel based alloys produce corrosion products, which are harmful to the human body (Brar *et al.*, 2009).

Pure magnesium (Mg) was indicated as suitable candidate for temporary implant, however, the major drawback of Mg is its low corrosion resistance which results to low mechanical strength in the physiological environment. Alloying elements can be added to increase the strength of pure Mg but alloying elements should be selected carefully to maintain the Mg biocompatibility (Brar *et al.*, 2009).

Magnesium and its alloys are biodegradable metals and exhibit improved mechanical properties and corrosion resistance. However most of the reported biomedical magnesium alloys contain aluminum and/or rare earth (RE) elements. Al is harmful to neurons, osteoblasts, and also associated with dementia and could lead to hepatotoxicity (Li and Zheng, 2013). Other alloying elements such as Zirconium (Zr) may lead to lung, liver and breast cancer (Song, 2007). With the purpose of searching for suitable alloying elements for biomedical magnesium alloys, researchers demonstrated that Calcium (Ca) and Zinc (Zn) could be appropriate candidates.

Zinc is one of the essential elements in human body that also provide mechanical strengthening in Mg-based alloys. Zinc can improve mechanical properties of magnesium alloys through precipitation strengthening. Furthermore, zinc is one of the most abundant nutritionally essential elements in the human body, and has basic safety for biomedical application. Moreover, RE can strengthen the material by solid solution strengthening by forming complex intermetallic phases with Al or Mg. These intermetallic phases act as obstacles for the dislocation movement at elevated temperatures and cause precipitation strengthening (Li and Zheng, 2013).

Calcium is one of the main elements in the human bone and release of Mg and Ca may improve bone healing. Calcium contributes to solid solution strengthening and precipitation strengthening. It also acts to some extent as a grain refining agent and additionally contributes to grain boundary strengthening (Witte *et al.,* 2008). The effect of Ca on corrosion resistance of Mg-Zn with addition of RE is very vague for biomedical applications. Thus, there is a need to investigate the effect of Ca addition on Mg-Zn-RE corrosion behavior.

1.2 Problem Statement

Stainless steels, Co-based alloys and titanium alloys are widely used in hard-tissue implants, especially in load-bearing applications, owing to their high strength, ductility and good corrosion resistance. With regard to biomedical implants, such as plates, screws and pins, used to repair serious bone fracture, it is desirable to use materials that can degrade in the physiological environment so that a subsequent surgical procedure to remove the implants from the human body after the tissues have healed is not necessary. Repeated surgery increases morbidity and health costs.

Magnesium and its alloys which are chemically active can degrade naturally in the physiological environment by corrosion and have high potential candidates in biodegradable hard-tissue implants. Alloying elements play important roles in magnesium alloys and the mechanical properties are usually the primary consideration when introducing alloying elements to the materials. Elements such as zinc (Zn), rare earth (RE) and calcium (Ca) are often added to Mg to improve on its corrosion behavior and at the same time provide adequate mechanical strength to be used as body implants.

1.3 Objective of the Research

The objective of this research is to investigate the effect of calcium additions on the microstructure, degradation behavior and corrosion properties of Mg-Zn-RE-*x*Ca alloys in simulated body fluid (Kokubo solution).

1.4 Scope of the Research

The scopes of the research are:

(i) Mg-2.2Zn-3.7RE-*x*Ca (*x* = 0, 0.5, 1.5, 3 and 6) alloys were prepared by casting method.

(ii) The specimens were subjected to microstructural analysis using optical microscopy (OM), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), scanning electron microscopy and energy dispersive X-ray spectroscopy (EDS) and Fourier transformed infrared spectroscopy (FTIR) techniques.

(iii) Mechanical property namely hardness was examined using Vickers hardness test.

(iv) The corrosion resistance was examined in-vitro by potentiodynamic polarization test, pH variation and immersion test in simulated body fluid (Kokubo solution) at room temperature.

REFERENCES

Agrawal, C. M. (1998). Reconstructing the Human Body using Biomaterials. *JOM*, 31–35

Atrens, A., Liu, M. and Zainal, A. N. (2011). Corrosion Mechanism Applicable to Biodegradable Magnesium Implants. *Materials Science and Engineering B*, 176, 1609-1636.

Avedesian, M. M. and Baker, H. (1999). Magnesium and Magnesium Alloys. *ASM Specialty Handbook*, *ASM International, Materials Park*, OH, 3–6.

Bakhsheshi-Rad, H. R., Abdul-Kadir, M. R., Idris, M. H. and Farahany, S. (2012). Relationship between the Corrosion Behavior and the Thermal Characteristics and Microstructure of Mg–0.5Ca–xZn alloys. *Corrosion Science*, 64, 184–197.

Brar, H. S., Platt, M. O., Sarntinoranont, M., Martin, P. I. and Manuel, M. V. (2009). Magnesium as a Biodegradable and Bioabsorbable Material for Medical Implant. *Journal of the Minerals, Metals, and Material Society*, 61(9), 31-34

Cai, S., Lei, T., and Li, N. (2012). Effects of Zn on Microstructure, Mechanical Properties and Corrosion Behavior of Mg–Zn Alloys. *Materials Science and Engineering C*, 32, 2570-2577.

Callister, W. D. (2007). Materials Science and Engineering: An Introduction, *Seventh Ed. John Wiley and Sons*.

Chiu K.Y., Wong M.H., Cheng F.T., and Man H.C. (2007). Characterization and Corrosion Studies of Fluoride Conversion Coating on Degradable Mg Implants. *Surface & Coatings Technology*, 202, 590-598.

Coy, A. E., Viejo, F., Skeldon, P. and Thompson, G. E. (2010). Susceptibility of Rare Earth-Magnesium Alloys to Micro-Galvanic Corrosion. *Corrosion Science*, 52, 3896-3906.

Disegi, J. and Eschbach, L. (2000). Stainless Steel in Bone Surgery. *Injury*, 31, D2-D6.

Dobrzañski, L. A., Król, M., Tañski, T. and Maniara, R. (2008). Thermal Analysis of the MCMgAl9Zn1 Magnesium Alloy. *Archives of Materials Science and Engineering*, 34, 113-116.

Du, H., Wei, Z., Liu, X. and Zhang, E. (2011). Effects of Zn on the Microstructure, Mechanical Property and Bio-corrosion Property of Mg-3Ca Alloys for Biomedical Application. *Materials Chemistry and Physics*, 125, 568-575.

Emadi, D., Whiting, L. V., Nafisi, S. and Ghomashchi, R. (2005). Application of thermal analysis in quality control of solidification process. *Journal of Thermal Analysis and Calorimetry*, 81, 235-242.

Fahamin, A, Tabrizi, B. and Ebrahimi-Kahrizsangi, R. (2012). Synthesis of Calciumphosphate-based Composite Nanopowders by Mechanochemical Process and Subsequent Thermal Treatment. *Ceramics International*. 38, 6729-6738.

Fathi, M. H., Salehi, M., Saatchi, A., Mortazavi, V. and Moosavi, S. (2003). In Vitro Corrosion Behavior of Bioceramic, Metallic and Bioceramic–Metallic Coated Stainless Steel Dental Implants. *Dental Materials*, 19(3), 188-198.

Geetha, M., Singh, A., Asokamani, R. and Gogia, A. (2009). Ti-based Biomaterials, The Ultimate Choice for Orthopaedic Implants–A Review. *Progress in Materials Science*, 54(3), 397-425.

Gu, X. N. and Zheng, Y. F. (2010). A Review on Magnesium Alloys as Biodegradable Materials. *Front. Mater. Sci. China*, 4(2), 111-115.

Gu, X., Zheng, Y. and Cheng, Y. (2009). In Vitro Corrosion and Biocompatibility of Binary Magnesium Alloys. *Biomaterials*, 30, 484-498.

Guo K.W. (2010). A Review of Magnesium/ Magnesium Alloys Corrosion and Its Protection. *Recent Patents on Corrosion Science*, 2, 13-21.

Hallab, N., Merritt, K. and Jacobs, J. J. (2001). Metal Sensitivity in Patients with Orthopaedic Implants. *The Journal of Bone & Joint Surgery*, 83(3), 428-428.

Handbook, A. S. M. (1990). Vol. 2. *ASM, Materials Par, OH*.

Hashemi N., and Clark, J.B. Phase diagrams of binary magnesium alloy. ASM International; 1988.

Hermawan, H., Dube, D. and Mantovani, D. (2010) Developments in Metallic Biodegradable Stents. *Acta Biomaterialia*, 6, 1693-1697.

Hin, T.S. (2004). Engineering Materials for Biomedical Applications. *Singapore: World Scientific*.

Hoffman, B. (1996). Biomaterials Science: An Introduction to Materials in Medicine. *Academic Press*.

Huang, Z. H., Liang, S. M., Chen, R. S. and Han, E. H. (2009). Solidification Pathways and Constituent Phase of Mg-Zn-Y-Zr Alloys. *Journal of Alloys and Compounds*, 468, 170-178.

Jun, J. H., Park, B. K., Kim, J. M., Kim, K. T. and Jung, W. J. (2007). Microstructure and Tensile Creep Behavior of Mg-Nd-RE-Ca Casting Alloys. *Key Engineering Materials*, 345-346, 557-560

Kainer, K. U., Srinivasan, P. B., Blawert, C. and Dietzel, W. (2010). Corrosion of Magnesium and Its Alloys. *Shreir's Corrosion*, 2011-2041.

Kannan, M. B. and Dietzel, W. (2012). Pitting-Induced Hydrogen Embrittlement of Magnesium–Aluminium Alloy. *Materials and Design*, 42, 321-326.

Kirkland, N. T., Lespagnol, J., Birbilis, N. and Staiger, M. P. (2010). A Survey of Biocorrosion Rates of Magnesium Alloys. *Corrosion Science*, 2010. 52: 287-291.

Levi, G., Avraham, S., Zilberov, A. and Bamberger, M. (2006). Solidification, Solution Treatment and Age Hardening of a Mg–1.6 wt.% Ca–3.2 wt.% Zn alloy. *Acta Materialia*, 54, 523-530.

Li, N. and Zheng, Y. (2013). Novel Magnesium Alloys Developed for Biomedical Application: A Review. *J. Mater. Sci. Technol.*, 1-14.

Li, Z., Gu, X., Lou, S. and Zheng, Y. (2008). The development of binary Mg-Ca alloys for use as biodegradable materials within bone. *Biomaterials*, 29, 1329-1344.

Long, M. and Rack, H. J. (1998). Titanium Alloys in Total Joint Replacement-A Materials Science Perspective. *Biomaterials*, 19(18), 1621-1639.

Matsubara, H., Ichige, Y., Fujita, K., Nishiyama, H. and Hodouchi, K. (2013). Effect of Impurity Fe on Corrosion Behavior of AM50 and AM60 Magnesium Alloys. *Corrosion Science*, 66, 203-210.

Meng, E. C., Guan, S. K., Wang, H. X. and Wang, L. G. (2011). Effect of Electrodeposition Modes on Surface Characteristics and Corrosion Properties of Fluorine-doped Hydroxyapatite Coatings on Mg-Zn-Ca alloy. *Applied Surface Science*, 257, 4811-4816.

Mudali, U. K., Sridhar, T. M. and Baldev, R. (2003). Corrosion of Bio-Implants. *Sadhana*, 28, 601-637.

Mueller, W. D. and Lucia, N. M. (2010). Critical discussion of the results from different corrosion studies of Mg and Mg alloys for biomaterial applications. *Acta Biomaterialia*, 6, 1749-1755.

Peter, B. and Maurus, M. D. (2004). Bioabsorbable Implant Material Review. *Operative Techniques in Sports Medicine*, 12(3), 158-160.

Shi, Z., Liu, M. and Atrens, A. (2010). Measurement of the corrosion rate of Magnesium Alloys using Tafel Extrapolation. Corrosion Science, 52, 579-588.

Song, G. (2007). Control of Biodegradation of Biocompatable Magnesium Alloys. *Corrosion Science*, 49, 1696-1701.

Song, G. L. and Song, S. Z. (2007). A Possible Biodegradable Magnesium Implant Material. *Advanced Engineering Materials*, 94, 298-302.

Song, Y., Hana, E. H., Shan, D., Yimb, C. D. and Youb, B. S. (2012). The Effect of Zn Concentration on the Corrosion Behavior of Mg-xZn Alloys. *Corrosion Science*, 65, 322-330.

Staiger, M. P., Pietak, A. M., Huadmai, J. and Dias, G. (2006). Magnesium and Its Alloys as Orthopedic Biomaterials: A review. *Biomaterials*, 27(9), 1728-1734.

Sumita, M., Hanawa, T. and Teoh, S. (2004). Development of Nitrogen-Containing Nickel-Free Austenitic Stainless Steels for Metallic Biomaterials - A Review. *Materials Science and Engineering: C,* 24(6), 753-760.

Wan, Y., Xiong, G. and Luo, H. (2008). Preparation and Characterization of a New Biomedical Magnesium–Calcium Alloy. *Materials & Design*, 29, 2034-2037.

Wang, Y., Wei, M. and Gao, J. (2008). Corrosion process of pure magnesium in Simulated Body Fluid. *Materials Letters*, 62, 2181-2184.

Witte, F., Hort, N., Vogt, C., Cohen, S., Kainer, K. U., Willumeit, R. and Feyerabend, F. (2008). Degradable Biomaterials Based on Magnesium Corrosion. *Current Opinion in Solid State and Materials Science*, 12, 63-72.

Xin, Y., Hub, T. and Chu, P. K. (2011). In vitro Studies of Biomedical Magnesium Alloys in a Simulated Physiological Environment: A Review. *Acta Biomaterialia*, 7, 1452-1459.

Yang, L. and Zhang, E. L. (2009). Biocorrosion Behavior of Magnesium Alloy in Different Simulated Fluids for Biomedical Application. *Mater Sci Eng* C, 29, 1691-1696.

Zainal-Abidin, N. I., Atrens, A. D. and Martin, D. (2011). Corrosion of High Purity Mg, Mg2Zn0.2Mn, ZE41 and AZ91 in Hank's Solution at 37°C. *Corrosion Scienc*e, 53, 3542-3556.

Zhang, E., Yin, D., Xu, L., Lei, Y. and Yang, K. (2009). Microstructure, Mechanical and Corrosion Properties and Biocompatibility of Mg–Zn–Mn Alloys for Biomedical Application. *Mater Sci Eng C*, 29, 987-993.

Zhang, S., Zhang, X., Zhao, C., Li, J., Song, Y., Xie, C., et al. (2010). Research on an Mg–Zn Alloy as a Degradable Biomaterial. *Acta Biomaterialia*, 6(2), 626-640.

Zhang, X., Yuan, G. Y., Mao, L., Niu, J. L. and Ding, W. J. (2012). Biocorrosion Properties of as-extruded Mg–Nd–Zn–Zr Alloy compared with Commercial AZ31 and WE43 Alloys. *Materials Letters*, 66(1), 209-211.

Zhou, T., Chen, D. and Chen, Z. H. (2008). Microstructures and Properties of Rapidly Solidified Mg-Zn-Ca Alloys. *Transactions of Nonferrous Metals Society of China*, 18, 101-106.

Zhou, T., Chen, D., Chen, Z. H. and Chen, J. H. (2009). Investigation on microstructures and properties of rapidly solidified Mg–6wt.% Zn–5 wt.% Ca–3 wt.% Ce Alloy. *Journal of Alloys and Compounds*, 475, L1-L4.