

STRUCTURAL, MECHANICAL AND CORROSION STUDY ON POSSIBLE BIODEGRADABLE MAGNESIUM ALLOYS

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Abstract

Due to the high biocompatibility of magnesium, magnesium based alloys are considered as suitable materials for the production of biodegradable implants such as the fixators of fractured bones or stents. The main insufficiencies of pure magnesium are lower yield and ultimate strength and high corrosion rate. As a consequence implants are degraded quickly and lose necessary mechanical properties in human organism before the tissue is sufficiently healed. Moreover, the problems with hydrogen bubbles and pH increase can cause serious medical complications. In present study, the mechanical and corrosion properties of pure Mg, Mg-4Nd and WE33 in the as-cast state are characterized. Polarization curves and EIS measurements were used to estimate corrosion resistance of studied materials. Although RE (Rare Earth) elements are often considered to improve mechanical properties and corrosion resistance of Mg based alloys, both Mg-4Nd and WE33 were characterized by significantly improved mechanical properties; however, corrosion resistance of both materials was strongly deteriorated compared to the pure Mg.

Keywords: Magnesium, rare-earth elements, tensile properties, corrosion behaviour

1. INTRODUCTION

Biodegradable materials may be gradually dissolved and absorbed in organism and also excreted without a production of toxic compounds. Such behaviour is very useful because no second surgery for taking out the implant, such as in the case of stainless steel, titanium and cobalt-based alloys, is needed [1, 2]. Competitive biodegradable polymer and ceramic materials are characterized by low mechanical properties, especially low strength and poor fracture toughness respectively. Metallic biomaterials offer superior mechanical properties in comparison with both above mentioned groups of materials, and therefore, they are more suitable for load-bearing applications [3]. In addition, mechanical properties are close to that of human bones which supports good healing process [1, 2]. Magnesium is considered as suitable structural element for biodegradable metal materials because it is an essential element for human organism where it plays important role in many biological processes. His recommended dietary allowance (RDA) for adults is 300-400 mg which is significantly higher amount compared to the other chemical elements [2, 4]. Possibility of using an alloy as biodegradable material depends in addition on the corrosion behaviour in human organism. Corrosion of magnesium alloys is accompanied by hydrogen release and pH increase.

Excessive corrosion rate can lead to the formation of hydrogen and local alkalization which may affect the pH dependant physiological reaction balances [2]. It is known that both mechanical properties and corrosion resistance can be improved by alloying with rare earth elements (RE) [5, 6]. In this work, structure states, mechanical properties and corrosion behaviour of pure Mg, Mg-4Nd and WE33 alloys in the as-cast state were investigated. Nd is considered as an element that can significantly improve the corrosion resistance and also mechanical properties of Mg alloys [7, 8]. WE33 represent material which contain lower amount of Nd than in Mg-4Nd alloy, however, presence of Y and other RE alloying elements can also lead to the improvement of mechanical properties and corrosion resistance. Moreover, the composition of this alloy is close to that of WE43 that has been a subject of many studies [9, 10]. These studies confirmed very good mechanical and corrosion properties of WE43 [9, 10].

2. EXPERIMENTAL

Cylindrical ingots of pure Mg, Mg-4Nd and WE33 were prepared by melting pure metals (99.9 %) in induction furnace under argon atmosphere and casting melts into cast-brass metal mould of 20 mm in diameter. Chemical composition of these ingots was studied by X-ray fluorescence spectrometry (**Table 1**). The structures of alloys were observed by light microscopy and scanning electron microscopy (Tescan Vega 3 LMU). Phase, chemical composition and surface morphology were studied by energy dispersion spectrometry (Oxford Instruments Inca 350) and X-ray diffraction (X'Pert Philips, 30 mA, 40 kV, X-ray radiation Cu K α). Structure studies were supplemented by Vickers hardness HV5 (loading 5kg) measurements. At least ten measurements were performed for each sample for statistic evaluation. Mechanical properties were also characterized on tensile tests that were carried out on rods with 10 mm in diameter and 100 mm in length on Lab Test 5.250SP1-VM. Corrosion behaviour was studied using electrochemical measurement. Both potentiodynamic tests and electrochemical impedance spectroscopy (EIS) were performed in physiological solution (PS) containing 9 g/l NaCl at initial pH 6.5 and at 37 °C. Prior to all test specimens were grinded to a P4000 SiC papers followed by rinsing in ethanol and drying in warm air. The ratio between sample surface area and volume of physiological solution was set on 50 ml/cm². A potentiostat in a standard three electrode setup was used. The sample with the shape of a cylinder with 10 mm in diameter and 15 mm in high, platinum wire and argentochloride electrode were used as working, counter and reference electrode, respectively. Electrodes were exposed to the SBF solution for 30 min before the potentiodynamic and EIS measurements. The cathodic polarization curves were obtained at a scan rate of 1 mV/s with a potential range from E_{ocp} (open circuit potential) to - 0.5 V vs E_{ocp} both at the beginning and at the end of 24 hour exposure. In EIS tests the signal amplitude of sinusoidal potential was 10 mV and a scan frequency ranged from 50 kHz to 0.025 Hz. The EIS results were than fitted by Gamry Elchem Analyst software. All experiments were repeated in order to obtain a good reproducibility.

Table 1 Chemical composition of the investigated materials (wt. %)

Alloy	Mg	Nd	Gd	Zr	Y	Dy	Zn	Al	Si	Fe	Ni	Cu
Mg	99.9	-	-	-	-	-	0.01	0.04	0.03	<0.004	<0.004	<0.004
WE33	93.96	2	0.48	0.33	2.98	0.25	0.01	-	-	0.012	<0.004	<0.004
Mg-4Nd	96.84	4.1	-	-	-	-	0.01	<0.01	<0.01	0.009	<0.004	<0.01

3. RESULT AND DISCUSSION

3.1 Structure and mechanical properties

Microstructures of the as-cast Mg, Mg-4Nd and WE33 alloy are shown on **Fig. 1**. Pure magnesium (**Fig. 1a, 1d**) was consisted of elongated grains with about 300 - 500 μ m in thickness and 1 - 1,5 mm in length. The microstructure of Mg-4Nd (**Fig. 1b, 1e**) alloy contains primary α -Mg dendrites and interdendritic eutectic phase. Dendrites were relatively fine with an average dendrite arm thickness of 10 μ m. Mg₁₂Nd phase was confirmed by both EDS measurements and XRD and also corresponds to the binary phase diagram of Mg-Nd system [11], where the maximum solid solubility of Nd in Mg is 3.6 wt. % at eutectic temperature and there is almost zero solubility at laboratory temperature. Due to the dendritic microsegregation, the concentration of Nd in dendrite cores and dendrite edges differed from 1.5 wt. % to 5 wt. %, respectively. Therefore, we assume that there is strongly oversaturated solid solution of Nd in α -Mg at dendrite edges where it surrounds Mg₁₂Nd eutectic phases. The microstructure of WE33 (**Fig. 1c, 1f**) was composed of α -Mg dendrites with about 25 μ m in diameter and interdendritic particles at grain boundaries containing about 10 wt. % Y, 14 wt. % Nd, 0.5 wt. % Zr, 0.7 wt. % of both Gd and Dy and 74.1 wt. % Mg. The Nd/Y ratio implies that the particles correspond to the ternary Mg₁₄Nd₂Y phase [12, 13] which was also confirmed by XRD analysis. EDS analysis showed a relatively high concentrations of alloying elements, particularly Zr, dissolved in the α -Mg dendrites. The

concentrations of Zr and Y in the cores of α -Mg dendrites were 0.88 and 1.97 wt. %, respectively. Nd was preferentially concentrated in intermetallic phases and at dendrite edges where its concentration reach almost 5 wt. %. On the contrary, the concentration of Nd in dendrite cores was about 0.2 wt. % and also Gd and Dy concentration was as low as 0.1 wt. %.

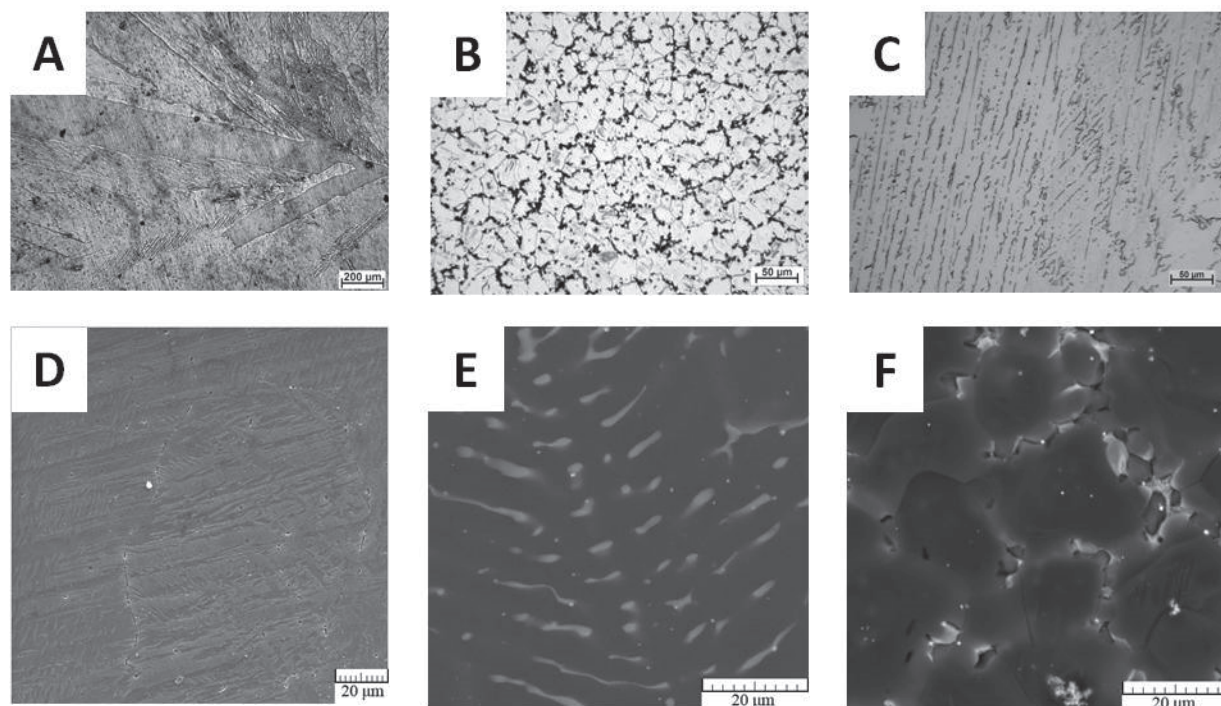


Fig. 1 The structure of studied materials (SEM): a) Mg (OM), b) Mg-4Nd (OM), c) WE33 (OM), d) Mg (SEM), e) Mg-4Nd (SEM), f) WE33 (SEM); OM - optical microscopy, SEM - scanning electron microscopy

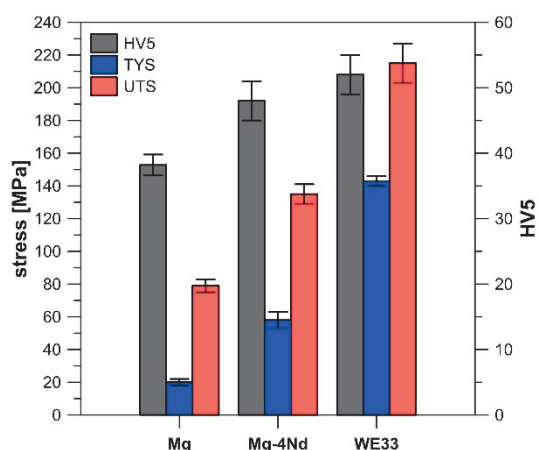


Fig. 2 Tensile properties and hardness of studied materials in the as-cast state

As for mechanical properties, Vickers hardness measurements and tensile tests were carried out. Both investigated alloys were characterized by higher hardness values and also higher tensile yield strength (TYS) and ultimate tensile strength (UTS) in comparison with pure Mg (**Fig. 2**). Three strengthening contributions can be expected in the studied alloys: 1. Hall-Petch (H-P) hardening, 2. solid solution hardening and 3. hardening by secondary intermetallic phases. Both alloys were characterized by much finer structure compared to the pure magnesium and therefore the H-P mechanism contribute significantly to higher

mechanical properties such as TYS and UTS of Mg-4Nd and WE33 (**Fig. 1**). The highest TYS and UTS for WE33 are probably connected with the finest structure from all studied materials. In addition WE33 contained higher amount of dissolved alloying elements in α -Mg which also improves the strength and hardness of material by solid solution hardening. Hardness and strength are also influenced by the volume fraction of secondary eutectic phases which are present in more quantities in WE33 alloy than Mg-4Nd. As a consequence hardness of studied materials increased in order Mg<Mg-4Nd<WE33.

3.2 Corrosion behaviour

Fig. 3 shows cathodic polarization curves and Niquist spectra of studied materials measured at the beginning of immersion test (solid lines) and after 24 hours of immersion in physiological solution (dashed lines). Data obtained by EIS were fitted by equivalent circuits that are showed on **Fig. 4**. The most important obtained data from both polarization curves and EIS spectra are shown in **Tab. 2**. It is evident that both Mg-4Nd and WE33 were characterized by higher values of corrosion potential at the beginning of exposure. Alloying elements are nobler than magnesium, and therefore, they shift corrosion potential to more positive values compared to pure magnesium. The corrosion potential is also increased during 24 hour immersion test which is connected with the presence of the corrosion products on the surface of material. These products were composed of $Mg(OH)_2$. It can be seen from **Table 2** that corrosion potentials of all studied materials are almost similar after 24 hours of immersion in physiological solution; however, corrosion rates represented by corrosion current densities are different. According to these results WE33 alloy should be characterized by the highest corrosion rate. Unfortunately cathodic branch of WE33 was significantly curved which does not allow the exact extrapolation of Tafel region and also significantly deteriorate the estimation of corrosion current density.

Fig. 3b illustrates the Niquist spectra of studied alloys at the beginning and at the end of 24 hour immersion test. In close proximity, with increasing value of real part of impedance corrosion resistance is increased. Therefore, magnesium is characterized by the lowest corrosion rate from studied alloys. Obtained spectra are characterized by the capacitive arc at high frequencies, capacitive arc at medium frequencies and inductive loop at low frequencies. Capacitive arc in high frequencies is attributed to the charge transfer resistance (R_{CT}) and double layer capacitance (C_{dl}) at the interface of solution and the surface of material. Capacitive arc in the middle frequencies results from the effects of surface film and C_f and R_f also represent the capacitance and resistance of corrosion products. Due to the depressed semicircles, constant phase elements CPE_{dl} and CPE_f were used to model obtained spectra instead of C_{dl} and C_f respectively (**Fig. 4**). The inductive loop is associated with the formation, adsorption and desorption of corrosion product on the surface [14]. L and R_L are designated as inductance and corresponding resistance respectively. Finally, in the equivalent circuit model, R_s represents the solution resistance between the reference electrode and working electrode. R_{CT} and R_f are the most important values because they represent corrosion resistance of material. Magnesium is in this case characterized by the highest R_{CT} and R_f and also the highest corrosion resistance from studied materials. On the contrary, R_{CT} and especially R_f values for Mg-4Nd and WE33 are significantly decreased compared to pure Mg. Although, rare earth elements (RE) are considered as suitable elements to improve corrosion resistance of Mg, obtained results showed that both studied alloys are dissolved faster than pure Mg. Due to the fact that the corrosion rate of pure Mg is insufficient and cause excessive release of hydrogen during in-vitro and in-vivo tests, studied alloys do not satisfy the requirements for applications as biodegradable materials. Increased degradation rate can be partially connected with the presence of some Fe in the materials which can significantly increase corrosion rate. Another reason can be connected with the presence of more noble intermetallic phases that acts as cathodic sites and increase the corrosion rate of α -Mg. Both these effects does not occur in the case of pure Mg. Slightly higher corrosion resistance of WE33 alloy compared to Mg-4Nd is probably connected with higher concentration of RE in α -Mg because these elements are known to improve the corrosion resistance of Mg alloys [15]. It is worth mentioning that real part of impedance and also R_{CT} and R_f increased during 24 hour immersion test. This is connected with the formation of corrosion products layer on the surface of materials.

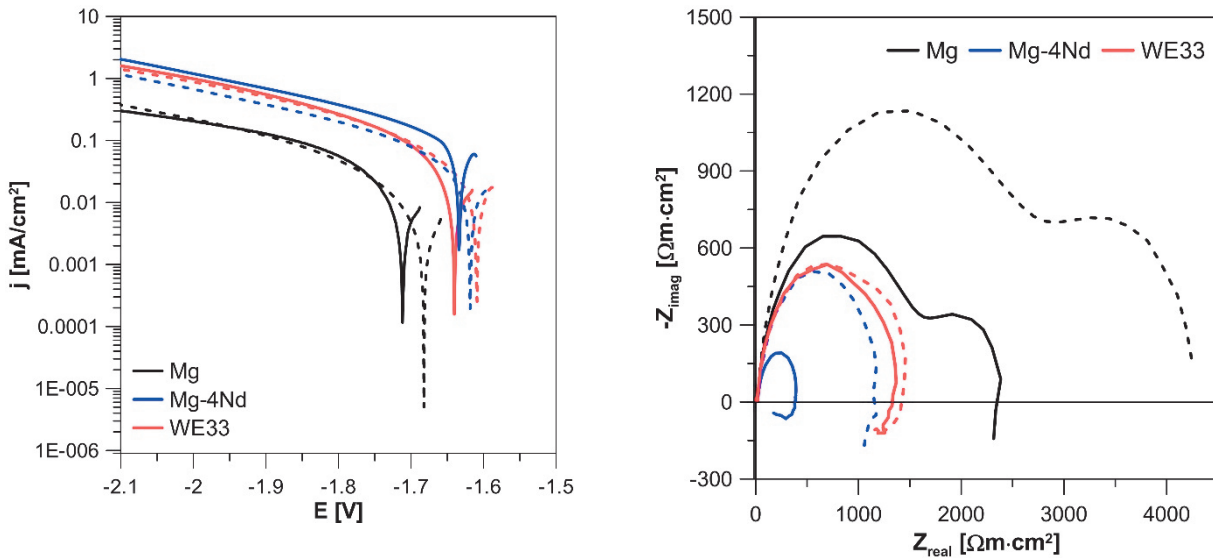


Fig. 3 Potentiodynamic curves and Nyquist spectra of studied alloys (Solid lines correspond to the state at the beginning of exposure and dashed lines correspond to the state after 24 hour immersion in physiological solution)

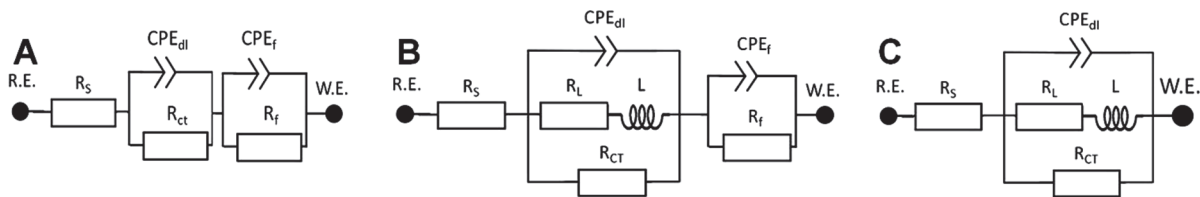


Fig. 4 Equivalent circuit models used for the characterization of EIS data obtained after 24 hour immersion in PS. Models were used as follows: a) pure Mg, b) WE33 E, c) Mg-4Nd

Table 2 Data obtained from polarization curves and Nyquist spectra after immersion of specimens in physiological solution for 24 hours

	polarization curves		EIS	
	E_{cor}	j_{cor} [mA/cm ²]	R_{CT} [Ω·cm ²]	R_f [Ω·cm ²]
Mg	-1.68	$4 \cdot 10^{-5}$	2436	1877
Mg-4Nd	-1.62	$6 \cdot 10^{-5}$	1163	
WE33	-1.61	$1 \cdot 10^{-3}$	1178	309

CONCLUSION

Mechanical properties and corrosion resistance of pure Mg, Mg-4Nd and WE33 were studied. Our results confirmed that addition of RE significantly improved the mechanical properties of magnesium, however corrosion behaviour was deteriorated. Two main reasons are considered:

- 1) The presence of high amount of intermetallic phases in the as-cast alloys which stimulate the galvanic corrosion and also affects the corrosion resistance.
- 2) The presence of impurities, such as Fe that can also significantly reduce the corrosion resistance.

Studied alloys fulfil partially the requirements for applications as biodegradable materials in the case of mechanical properties; however, corrosion properties are quite poor and undesirable hydrogen release and excessive rate of implant degradation prevent the application of these materials in presented state.

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