INFLUENCE OF MECHANICAL AND THERMAL TREATMENT ON MECHANICAL AND BIODEGRADATION PROPERTIES OF MAGNESIUM ALLOYS

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Abstract
Magnesium is an essential element for human organism that works as a cofactor for some enzymes, participates in DNA or RNA synthesis and support bone growth. Mechanical properties, such as density and modulus of elasticity, are close to that of bones. Therefore, magnesium is considered as a suitable element for manufacture of biodegradable implants. The main insufficiency of Mg and Mg-based alloys is still too high corrosion rate, which mean that Mg-based implant are degraded or lose necessary mechanical properties in human organism before the tissue is sufficiently healed. Different methods can be used to increase corrosion resistance in body fluid, such as suitable alloying especially by Rare Earth Elements (REE), modification of structure by mechanical or thermal treatment and different surface treatment. In this study, mechanical and corrosion properties of pure magnesium, AZ31 and WE43 magnesium alloys in the as-cast state and wrought condition were studied. Both alloys are considered as candidates for production of implant materials. The as-cast states of studied alloys were characterized by significantly improved mechanical properties compared to pure magnesium and these properties were further improved by processing of the as-cast alloys. Based on the both mechanical properties and corrosion resistance, WE43 alloy seems the most prospective material for medical applications.

Keywords: magnesium, biodegradable materials, mechanical properties, corrosion resistance

1. INTRODUCTION
Magnesium alloys are suitable candidates for biodegradable medical implants, such as fixation devices for fractured bones or stents [1]. Such materials can be gradually dissolved and absorbed in organism without a production of toxic compounds [2]. Magnesium is an essential element for human organism and plays an important role in many biological processes. However, high demands are required in the case of mechanical properties and corrosion resistance of possible Mg-based biodegradable materials. In this case, magnesium alloys possess good mechanical properties, such as tensile and compressive yield strength, ultimate tensile and compressive strength, elongation or modulus of elasticity that is very close to that of bones which also support good healing process [1, 2]. The main problem of magnesium and its alloys is quite poor corrosion resistance. Excessive corrosion rate leads to the higher hydrogen release and pH increase. Both phenomena significantly affect healing process near the implant [2-4].

Alloying with Al and rare earth elements (REE) can improve the mechanical properties and also corrosion resistance of magnesium alloys [5-7]. Therefore, structure states, mechanical properties and corrosion behaviour of pure Mg, AZ31 and WE43, both in the as-cast and wrought state were investigated in this work. The selected materials have already been the subject of research and are considered as possible candidates for biodegradable materials [8-10]. The aim of this work was to directly compare the properties of studied alloys and find the relation between structure conditions, mechanical and corrosion properties.
2. EXPERIMENTAL

In this work, we studied structures, mechanical and corrosion properties of pure Mg, AZ31, WE43 in the as-cast state and also AZ31 in the wrought state and WE43 in the wrought state in combination with subsequent T5 thermal treatment. Alloys were prepared in Magnesium Elektron. To ensure comparable state of the as-cast materials, rods with 20 mm in diameter and 150 mm high were prepared by remelting obtained ingots in induction furnace under protective argon atmosphere and casting the melt into the brass mould. Alloys in the as-cast state are designated as AZ31 F and WE43 F, alloys in the wrought conditions are designated as AZ31 E and WE43 E. Chemical composition of studied materials determined by XRF is shown in Table 1. The structures of alloys were observed by SEM (Tescan Vega 3 LMU). Phase, chemical composition and surface morphology were studied by energy dispersion spectrometry (Oxford Instruments Inca 350) and XRD (X'Pert Philips, 30 mA, 40 kV, X-ray radiation Cu Kα). Structure studies were supplemented by Vickers hardness measurements with loading 5kg (HV5). Tensile tests 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 measurements. 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 PS solution for 30 min before the first potentiodynamic and EIS measurements. The cathodic polarization curves were obtained at a scan rate of 1 mV/s with a potential range from Eoc (open circuit potential) to – 0.5 V vs Eoc both at the beginning and at the end of 24 hour immersion test. EIS measurements were carried every hour during 24 hour immersion test. 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 Analist software. All experiments were repeated in order to obtain a good reproducibility.

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

<table>
<thead>
<tr>
<th>wt.%</th>
<th>Y</th>
<th>Nd</th>
<th>Gd</th>
<th>Dy</th>
<th>Zr</th>
<th>Al</th>
<th>Zn</th>
<th>Mn</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Si</th>
<th>Mg</th>
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<tbody>
<tr>
<td>Mg</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;0.01</td>
<td>-</td>
<td>&lt;0.01</td>
<td>0.002</td>
<td>-</td>
<td>0.01</td>
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<tr>
<td>WE43</td>
<td>4.0</td>
<td>2.3</td>
<td>0.48</td>
<td>0.25</td>
<td>0.42</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
<td>0.002</td>
<td>0.001</td>
<td>-</td>
<td>0.01</td>
<td>bulk</td>
</tr>
<tr>
<td>AZ31</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.1</td>
<td>0.79</td>
<td>0.24</td>
<td>&lt;0.01</td>
<td>0.002</td>
<td>0.0006</td>
<td>0.01</td>
</tr>
</tbody>
</table>

3. RESULTS AND DUSCUSSION

3.1 Structure and mechanical properties

Structures of the as-cast Mg, WE43 and AZ31 and wrought WE43 and AZ31 alloy are shown on Fig. 1. Pure magnesium was consisted of elongated grains with about 300 – 500 μm in thickness and 1 – 1.5 mm in length. Structure of the as-cast WE43 alloy (Fig. 1b) contained primary α-Mg dendrites with about 25 μm in diameter and interdendritic eutectic phase. Interdendritic phase contained 3.8 at.% Y, 5.6 at.% Nd, 0.1 at.% Zr, about 0.05 at.% of both Gd and Dy and 90.5 at.% Mg. Interdendritic particles were quite small; therefore, EDS analysis were partially influenced by surrounding α-Mg. However, the Nd/Y ratio implies that the particles correspond to the ternary Mg₁Nd₂Y phase [11, 12]. 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 0.5 and 0.3 at.%, respectively. Nd was preferentially concentrated in intermetallic phases and at dendrite edges where its concentration was about 0.5 at.%. On the contrary, the concentration of Nd in dendrite cores was about 0.03 at.% and also Gd and Dy concentration was lower.
The structure of WE43 in the wrought condition and after T5 heat treatment (Fig. 1c) consisted of large equiaxed grains with about 80 μm in diameter. Majority of secondary phases was dissolved during thermomechanical processing and dendritic microsegregation disappeared. The average concentration of alloying elements was 1 at.% for Y, 0.35 at.% for Nd, 0.07 at.% for Gd, 0.05 at.% for Dy and 0.2 at.% for Zr. Some small intermetallic phases that occurred sporadically in the structure contained high amount of Y and remained in the structure both at grain boundaries and inside the grains. These phase contained about 16 at.% of Y and 1.5 at.% of Nd and corresponds to the Mg24Y5 phase [13]. Structure of the as-cast AZ31 alloy (Fig. 1d) contained primary α-Mg dendrites and interdendritic eutectic phase with about 25 at.% of Al, 5 at.% of Zn and 0.02 at.% of Mn which correspond to the Mg17Al12 [13]. The alloy was characterized by obvious dendritic microsegregation. The concentration of Al ranged from 1 to almost 5 at.% for Al and from 0.15 to 0.45 at.% for Zn for dendrite cores and dendrite edges respectively. AZ31 in the wrought state was characterized by homogenous structure with average Al, Zn and Mn concentration 2.91, 0.34 and 0.4 at.% respectively. Only at some areas small Mg17Al12 phases which were ranked in the direction of extrusion were observed (Fig. 1e).

Mechanical properties were studied by Vickers hardness measurements and tensile tests. All investigated materials were characterized by higher hardness values and also higher tensile yield strength (TYS) and ultimate tensile strength (UTS) compared with pure Mg (Fig. 2). This is considered for three main reasons: 1. All materials were characterized by finer structure compared to the pure Mg in the as-cast state. Therefore, Hall-Petch (H-P) strengthening mechanism cause increase in the TYS, UTS and also HV5. This also significantly improved the mechanical properties of wrought AZ31 which was characterized by the average grain size about 10 μm. 2. All alloys contained some amount of alloying elements in the α-Mg which improved the mechanical properties by solid solution strengthening mechanism. This contribution is assumed especially in the case of wrought WE43 because in this state, alloy contained high amount of alloying elements in α-Mg and majority of secondary phases that were observed in the as-cast state were dissolved during processing of WE43. Due to the fact that this alloy was also after the T5 treatment, some very small precipitates that are not observable using SEM can be presented in the structure. These precipitates can cause increase in hardness and TYS or UTS of WE43 which is denoted as 3. strengthening by secondary intermetallic phases. In the as-cast state, both AZ31 and WE43 contained intermetallic particles in the structures which also improved the hardness, TYS and UTS values compared to the pure Mg. During processing routes of AZ31 and WE43, secondary phases were partially dissolved to the α-Mg and recrystallization took place. Therefore the mechanical properties of both wrought alloys are preferentially affected by Hall-Petch (H-P) strengthening and solid solution strengthening mechanisms.
Fig. 1 Structure of studied materials (SEM): a) Mg, b) WE43 F, c) WE43 E, d) AZ31 F, e) AZ31 E.

Fig. 2 Tensile properties and hardness of studied materials.

3.2 Corrosion behaviour

Fig. 3 shows the 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 date obtained from both polarization curves and EIS measurements are shown in table 2.

It can be seen from Fig. 3 that AZ31 F and AZ31 E were both at the beginning of exposure and after 24 hours of immersion characterized by higher values of corrosion potential compared to the pure Mg. In this case, aluminium and zinc are much nobler metals than magnesium [14], and therefore, they shift the corrosion potential to more positive values compared to the pure Mg. Also the corrosion potential of WE43 F alloy was at slightly higher values compared to the pure Mg; however, the corrosion potential of the wrought WE43 E alloy was even lower compared to the pure Mg. For all studied materials, the corrosion potential increased during 24 hour immersion test which is connected with the formation of the corrosion products containing Mg(OH)₂ on the surface [15]. Corrosion current densities that were determined by the extrapolation of Tafel region are very similar and they also do not provide useful information about differences in the corrosion rates of studied materials. The reason can be in the curved cathodic branch of polarization curves which does not allow the exact extrapolation of Tafel region and also significantly deteriorate the estimation of corrosion current density. Cathodic curves represent the cathodic processes on the surface of alloy during corrosion processes which are dominated by hydrogen evolution. Therefore, higher current densities at cathodic branches are connected with higher hydrogen release. In this case pure Mg, and WE43 in the wrought condition should be characterized by the lowest corrosion rates. On the contrary, AZ31 in both states were much less corrosion resistant.

Fig. 3 also illustrates the Niquist spectra of studied alloys at the beginning and at the end of 24 hour immersion test. Based on the alloy, obtained spectra are characterized by the capacitive arc at high
frequencies, capacitive arc in medium frequencies and inductive loop in low frequencies. Capacitive arc in high frequencies is attributed to charge transfer resistance ($R_{CT}$) and double layer capacitance ($C_{dl}$) at the interface of solution and the surface of material. Capacitive arc in 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 [16]. $L$ and $R_L$ are designated as inductance and corresponding resistance respectively. $R_S$ 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. Based on the fitting results WE43 E is characterized by the highest $R_{CT}$ and $R_f$ and also the highest corrosion resistance from studied materials (Table 2). On the contrary, $R_{CT}$ and $R_f$ values for WE43 F were significantly decreased compared even to the pure Mg. In the case of AZ31 F and AZ31 E only circuit with one time constant has been selected and obtained $R_{CT}$ values corresponds to the lowest corrosion resistance of the AZ31 alloys in both states. During 24 hour immersion test $R_{CT}$ and $R_f$ was increased for all materials. This is connected with the formation of corrosion products layer on the surface and it agrees well with the shifts of corrosion potentials during immersion test to more noble values. Obtained results showed that except WE43 E all studied alloys dissolved faster than the pure Mg. This can be partially connected with the presence of more noble intermetallic phases in the structure which acts as cathodic sites and increase the corrosion rate of $\alpha$-Mg [7]. Such phases were observed especially in the as-cast alloys. On the contrary, majority of such phases were dissolved in WE43 E. This means that the influence of microgalvanic cell is partially suppressed. Moreover, Y and other RE elements are known to be able to accumulate in the corrosion products and increase the protective character of formed surface layers [17]. This effect is probably supported by higher concentration of these elements in $\alpha$-Mg.

![Fig. 3 Potentiodynamic curves and Niquist 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.)](image)

![Fig. 4 Three equivalent circuit models used for the characterization of EIS data. Models were used as follows: a) for pure Mg and WE43 E, b) for WE43 F, c) for AZ31 F and AZ31 E.](image)
Table. 2 Data obtained from polarization curves and Niquist spectra after immersion of specimens in physiological solution for 24 hours.

<table>
<thead>
<tr>
<th></th>
<th>polarization curves</th>
<th>EIS</th>
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<tr>
<td></td>
<td>E_{cor} [V]</td>
<td>j_{cor} [mA/cm²]</td>
</tr>
<tr>
<td>Mg</td>
<td>-1.68</td>
<td>4·10⁻⁵</td>
</tr>
<tr>
<td>AZ31 F</td>
<td>-1.57</td>
<td>4·10⁻⁵</td>
</tr>
<tr>
<td>AZ31 E</td>
<td>-1.58</td>
<td>8·10⁻⁵</td>
</tr>
<tr>
<td>WE43 F</td>
<td>-1.64</td>
<td>8·10⁻⁵</td>
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<tr>
<td>WE43 E</td>
<td>-1.76</td>
<td>5·10⁻⁵</td>
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</table>

4. CONCLUSION

In present work mechanical properties and corrosion resistance of pure Mg, AZ31 and WE43, both in the as-cast and wrought condition, were studied. All alloys in the wrought and also as-cast condition were characterized by significantly improved mechanical properties compared to the pure Mg. Corrosion resistance of both AZ31 and WE43 in the as-cast state was very poor compared to the pure Mg. On the contrary, the results confirmed that WE43 in the wrought condition was characterized by the highest corrosion resistance. Structure conditions, especially occurrence of intermetallic phases are considered as the main reason responsible for differences in measured corrosion rates.

5. ACKNOWLEDGEMENT

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6. REFERENCES

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