EFFECT OF ECAP ON THE MICROSTRUCTURE, MECHANICAL AND CORROSION PROPERTIES OF Mg-Zn-Ca AND Mg-Zn-Ca-Mn BIODEGRADABLE ALLOYS

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Abstract

The Mg - 2.2-3.8 wt.% Zn - 0.3-0.7 wt.% Ca - 0-0.9 wt.% Mn alloys as a material for the production of biodegradable implants was investigated. Equal-channel angular pressing (ECAP) to improve the grain structure and mechanical properties of the alloys was used. The microstructure and phase composition of alloys were determined using scanning electron microscopy and energy dispersive X-ray spectroscopy. The phase diagrams and alloys phase composition were calculated using the Thermo-Calc software. For the alloy sample, a differential thermal analysis (DTA) was carried out. The mechanical properties and corrosion properties of ECAP processed alloys were investigated. In vitro corrosion test by hydrogen evolution method was carried out in Hank's solution. The alloys containing Mn were composed of primary solid solution (Mg), manganese particles (Mn) and eutectic (Mg) + (Mn) + $Ca_2Mg_6Zn_3$. The alloys without Mn were composed of primary solid solution (Mg) and eutectic (Mg) + $Ca_2Mg_6Zn_3$. The alloys have a wide equilibrium crystallization range of about 250 °C. The solute treatment of alloys leads to an increase of the zinc concentration in the (Mg) solid solution. Calcium and manganese are slightly soluble in (Mg) solid solution. The obtained samples of Mg-Zn-Ca and Mg-Zn-Ca-Mn alloys have ultimate strength (UTS) from 220 to 240 MPa, and elongation (El) from 17 to 29 % after ECAP. The corrosion test was executed for 192 hours. All investigated alloys showed approximately the same result. The manganese addition didn't affect the corrosion resistance of the investigated alloy after ECAP.

Keywords: Biodegradable magnesium alloys, Mg-Zn-Ca-Mn, Mg-Zn-Ca, ECAP, corrosion

1. INTRODUCTION

Biodegradable magnesium alloys are designed to provide temporary support and connectivity during the healing process in damaged tissue [1]. Those alloys gradually degrade and are replaced by own bone tissue when they are restored [1, 2]. Magnesium alloys are good material for the production of biodegradable implants combine a number of useful properties at a low cost. However, because of insufficient strength and corrosion resistance, these alloys do not always meet the requirements [3, 4]. The severe plastic deformation treatment (SPD) can improve the grain structure of metallic materials [5]. The most effective method of SPD is equal-channel angular pressing (ECAP) [6]. Some elements, for example Ca, Zn, Mn, lower the biodegradation rate of magnesium alloys [7]. Their use in combination with ECAP makes it possible to obtain biodegradable materials with good mechanical and corrosion properties.

Zinc is one of the most commonly used alloying elements in Mg and has very low neurotoxic effect [4, 8]. It is also known that calcium is a major component in human bone and calcium is also essential in chemical signaling with cells and Mg - Ca alloys did not induce toxicity to cells [9]. Therefore, the Mg alloys containing Zn and Ca are promising as biodegradable materials [9]. Addition of Zn from 1 to 6 wt.% increases the yield strength (YS) of the binary Mg-Zn alloy, but the optimum content of Zn is 4 wt.% [10, 11]. Calcium is a grain refiner for Mg based alloys [12] and improves the mechanical and corrosion properties of Mg - Zn alloys [13, 14]. The maximum addition of Ca in the Mg alloy with Zn does not exceed 0.5-1 wt.% [10, 15]. Mn also promotes grain refinement and improves tensile strength of magnesium alloys [15].

The goal of this work is to investigate the microstructure, mechanical and corrosion properties of Mg - Zn - Ca and Mg - Zn - Ca - Mn alloys in as-cast and ECAP states that are good candidates for using as biodegradable materials.

2. MATERIALS AND METHODS

For alloys preparation as raw materials commercial purity magnesium (99.9 wt.% Mg), zinc (99.98 wt.% Zn) and Mg - 30 wt.% Ca and Mg - 2.7 wt.% Mn own production master alloys were used. Melt prepared using induction furnace in a steel crucible under cover of carnallite flux. Cylindrical ingots with diameter of 35 mm were cast in a steel permanent mold. The chemical composition of alloys is presented in **Table 1**.

Table 1 The elements content in alloys (wt.%)

Alloys	**Mg**	**Zn**	**Ca**	**Mn**
MCZ1	Bal.	3.8	0.3	0.9
MCZ2	Bal.	2.2	0.7	-
MCZ3	Bal.	3.6	0.5	-
MCZ4	Bal.	2.2	0.4	0.8

Cylinders for ECAP by diameter of 20 mm were cut from ingots using spark cutting. The ingots were heat treated at 350 °C for 8 h.

The ECAP processing was carried out using a die with 20 mm diameter chanel and angle of 120°. The samples was processed for four passes in which the sample was rotated along its longitudinal axis to 180° after first pass and for 90° and 180° after second and third passes. Samples and die were preheated to 350 °C.

The Thermo-Calc software with thermodynamic database TCMG4 (TCS Mg-based Alloys Database version 4) for alloys phases composition calculation was used.

The Tescan Vega SBH3 Scanning Electron Microscope with EDS system Oxford for microstructure and phase composition analysis was used. The alloys chemical composition is determined by EDS analysis in metallographic sections surface by area of 1 mm^2. For each sample three areas are analyzed and mean elements content are calculated.

The solidification range of alloys obtained using differential thermal analysis (DTA) on differential scanning calorimeter Labsys (SETARAM).

Corrosion test was carried out on ECAP processed alloy samples. The disks having 12.5 mm diameter and 3.5 mm height were spark machined and grounded. The samples surface area was 3.8 cm^2. Samples were immersed in Hank's solution produced by "PanEco" company (Russian Federation) at 37 °C for 192 h. Hydrogen evolution was measured as a function of time and normalized to 1 cm^2 of specimens' surface area.

During corrosion test the change in time of Hank's solution pH was measured using pH211 Hanna Instruments pH meter. The volume of the Hank's solution was 400 ml for each alloy sample.

The ECAP processed alloy samples are spark machined for mechanical testing samples with 1.4x1 mm cross section and 12 mm length. Tensile tests were performed on the INSTRON 5569 universal testing machine.

3. RESULTS AND DISCUSSION

The alloys microstructures are shown in **Figure 1**. As-cast alloys MZC2 and MZC3 have similar microstructures, but the alloys MZC1, MZC4 differ. This is because MZC1 and MZC4 alloy contain Mn but MZC2 and MZC3 is Mn free. The presence of manganese in the alloy contributes to the formation of more branched dendrites. The alloys containing Mn (MZC1 and MZC4) were composed of primary crystals of magnesium solid solution (Mg), manganese particles (Mn) and eutectic (Mg) + (Mn) + $Ca_2Mg_6Zn_3$. The alloys without Mn (MZC2 and MZC3) were composed of primary solid solution (Mg) and eutectic (Mg) + $Ca_2Mg_6Zn_3$. In addition, at room temperature in accordance with phase composition calculation, there may exist a phase MgZn which can be formed during aging or after ECAP.

The alloys liquidus and solidus temperatures calculated using the Thermo-Calc software and measured by differential thermal analysis (DTA) are presented in **Table 2**.

Table 2 The temperature (calculated / measured) of liquidus (t_{liq}) and solidus (t_{sol}) for obtained alloys

Alloys	T_{liq}	T_{sol}	$\Delta T = T_{liq} - T_{sol}$
MCZ1	638/617	374/387	264/230
MCZ2	642/627	394/406	248/221
MCZ3	636/622	385/384	251/238
MCZ4	641/632	394/399	247/233

The obtained alloys have a wide equilibrium solidification range of about 250 °C. Measurements by DTA showed similar results. The DTA results for MZC1 and MZC4 alloys are shown in **Figure 2**. It can be seen that most of the solid is formed near the liquidus during solidification. This corresponds to the solid solution (Mg) formation. Close to the solidus temperature, a small amount the low-melting eutectic is formed, which will be concentrated along the dendrites boundaries. The melting of low-melting eutectic can lead to alloys samples destruction at ECAP process. The nonequilibrium solidus (**Figure 2**) is close to the calculated results (**Table 2**), so the heat treatment temperature was applied about 25 - 45 ° C below the equilibrium solidus.

The tensile properties of the obtained alloys after ECAP are shown in **Table 3**. It can be seen the tensile properties of alloys are similar and have ultimate strength (UTS) from 220 to 240 MPa, and elongation (El) from 17 to 29 % after ECAP. A promising way to increase the UTS is to increase the degree of deformation due to the more elaborate ECAP processing.

Table 3 - The tensile properties of the obtained alloys after ECAP

Alloys	*YS* (MPa)	*UTS* (MPa)	Elong. (%)
MZC1	90.4	219.7	20.2
MZC2	97.8	223.7	16.7
MZC3	78.0	238.9	28.6
MZC4	79.9	226.9	27.7

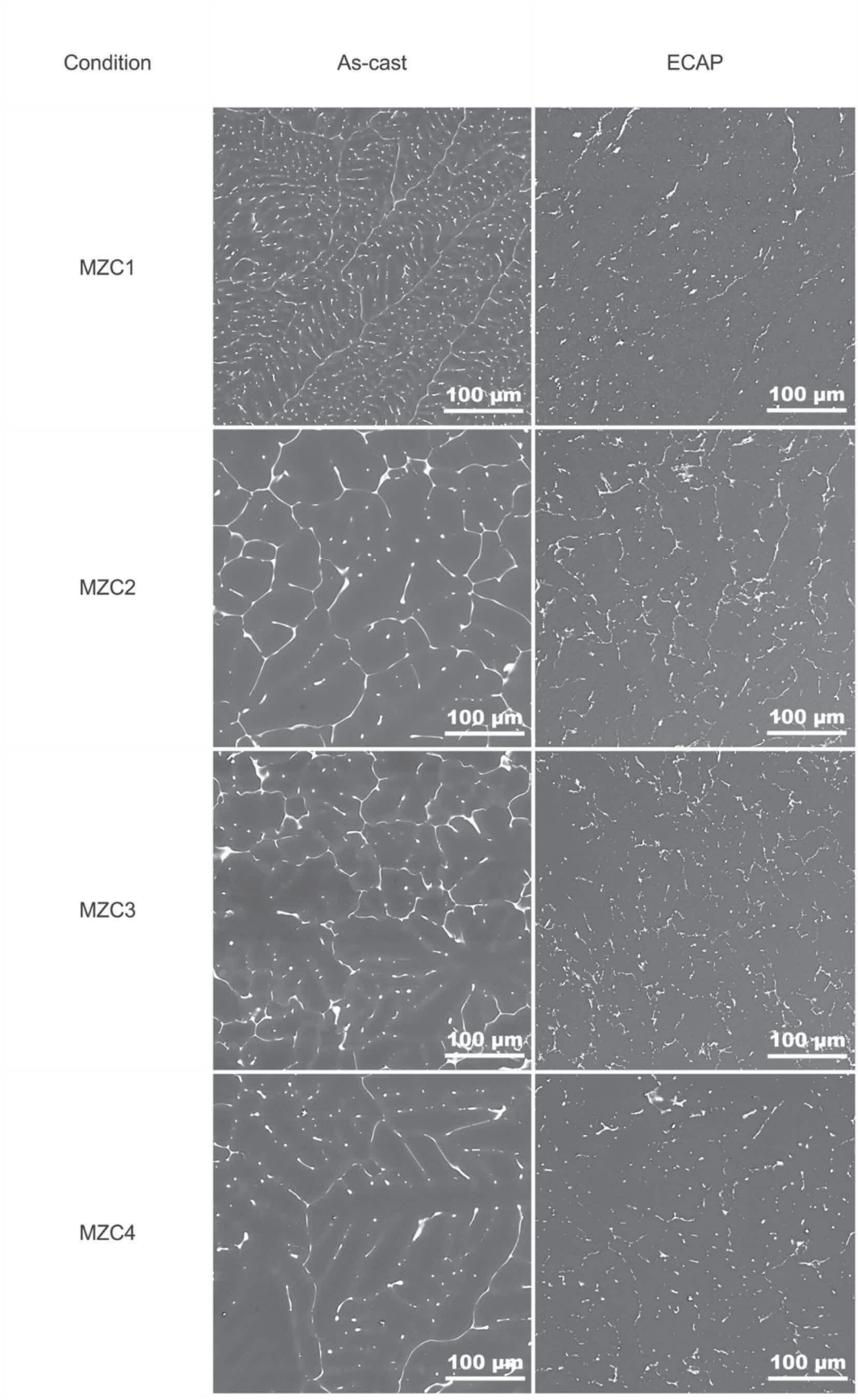

Figure 1 Microstructure of alloys in the as-cast condition (left), and after ECAP (right)

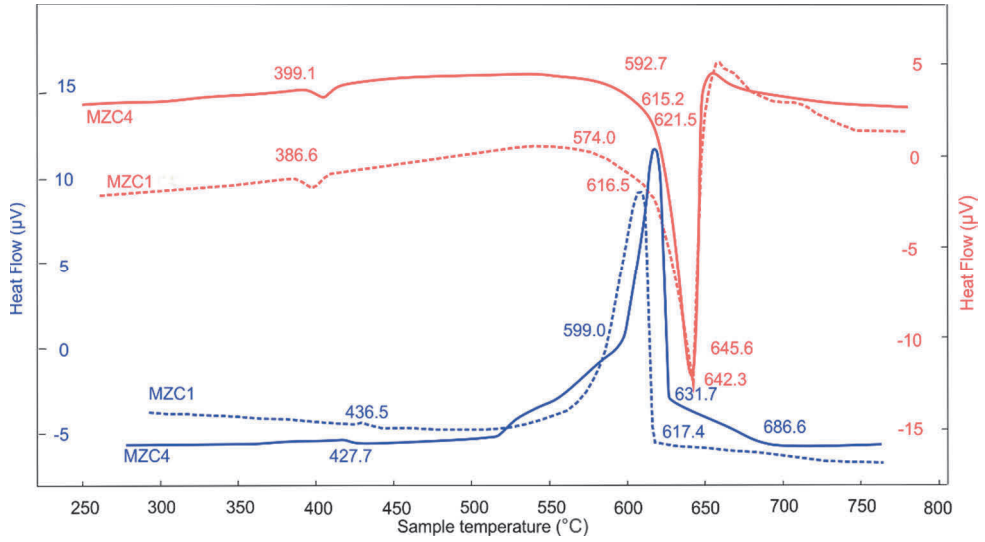

Figure 2 The DTA results for MZC1 (dotted line) and MZC4 (solid line) alloys. Blue is cooling line and red is heating line. Heating / cooling rate 10 K / min

The corrosion properties of the alloys after ECAP are shown in **Figure 3**. It can be seen that the corrosive properties of alloys are similar after 192 h in Hank's solution. The Hank's solution pH varied from 7.5 at the start corrosion test to 8.7 at the end. The increase Hank's solution pH is a consequence the OH^- ions accumulation due to the corrosion products formation, for example, $Mg(OH)_2$.

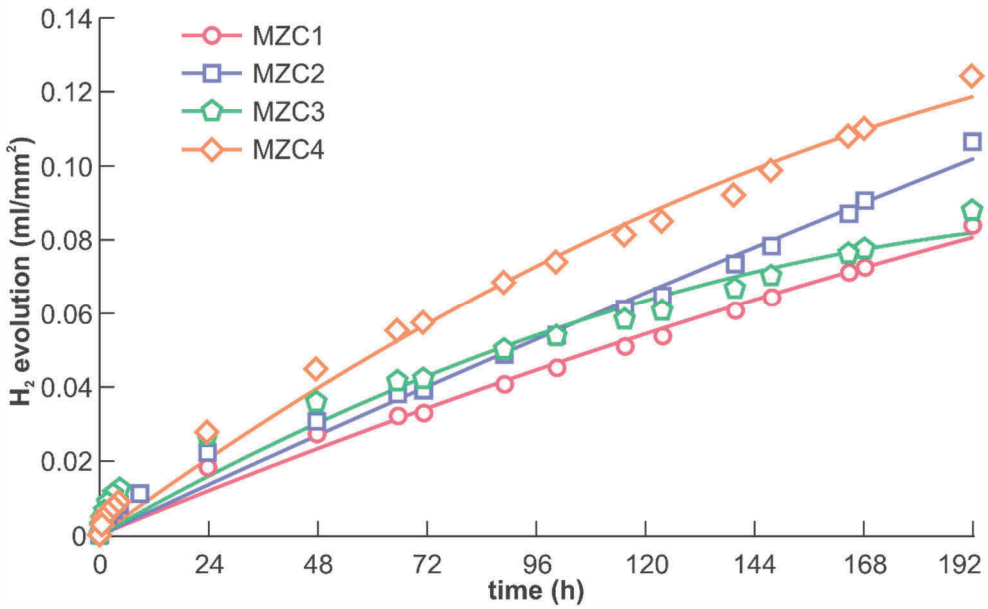

Figure 3 The alloys corrosion test results after ECAP

The hydrogen evolution was from 0.00063 to 0.00042 ml/mm^2·h and the maximum hydrogen evolution rate from 0.002 to 0.003 ml/mm^2·h was observed after the first 4 hours. This can be explained by the oxide film absence on alloys samples surface at the tests beginning. Then the hydrogen evolution rate decreased and was practically constant until the test end. It is known [16] the reaction of hydrogen evolution is controlled by reactants or products diffusion through the alloy surface film at solution pH ≤11. Therefore, a stable oxide film on the investigated alloys is formed for approximately 4 hours in the Hank's solution. It is possible to effectively control the alloy corrosion rate by changing the oxide film properties.

4. CONCLUSION

The tensile properties of Mg - 2.2-3.8 wt.% Zn - 0.3-0.7 wt.% Ca - 0-0.9 wt.% Mn alloys after ECAP are similar and have UTS from 220 to 240 MPa, YS from 80 to 98 MPa and El from 17 to 29 %. The alloys were composed of primary solid solution (Mg) and eutectic (Mg) + $Ca_2Mg_6Zn_3$. The Mn addition is causes the formation of small manganese particles (Mn) into magnesium solid solution (Mg) and eutectic (Mg) + (Mn) + $Ca_2Mg_6Zn_3$ formation. The investigated alloys have solidification range about 250 °C. The corrosion properties of the alloys after ECAP are similar after 192 h in Hank's solution for all alloys. The Hank's solution pH varied from 7.5 at the start corrosion test to 8.7 at the end. Manganese does not affect the corrosion and tensile properties of alloys.

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