MICROSTRUCTURE, MECHANICAL AND CORROSION PROPERTIES OF BIODEGRADABLE Mg-Ga-Zn-X (X = Ca, Y, Nd) ALLOYS

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Abstract

We investigate the new alloys of Mg-Ga-Zn-X system, where X = Ca, Y and Nd. These alloys can be used as biodegradable materials due to the low cytotoxicity of Zn and Ga and effectiveness of Ga against bone resorption, osteoporosis and Paget's disease. The microstructure and phase composition of alloys were determined using scanning electron microscopy and energy dispersive X-ray spectroscopy. The as-cast microstructure of Mg - 4 wt.% Zn - 4 wt.% Ga (Mg4Zn4Ga) alloy consists of magnesium solid solution (Mg) and two eutectic phases with composition $(Mg,Ga)_7Zn_3$ and $(Mg,Zn)_5Ga_2$. For the improvement of mechanical properties the severe plastic deformation technique named equal channel angular pressing (ECAP) was used. Microstructure, mechanical and corrosion properties of ECAP processed alloys were investigated. It was established that the grain sizes differ more than ten times in microstructure of Mg4Zn4Ga alloy after ECAP. The additions of 0.2 - 0.3 wt.% Ca, Y and Nd lead to formation of uniform-sized grains of 5 - 15 µm. Mentioned previously additions do not change the mechanical properties of Mg4Zn4Ga alloy and measured values of ultimate tensile stress (UTS) is 298 MPa, yield stress (YS) is 167 MPa and elongation (El) is 23 % for Mg4Zn4Ga alloy. The hydrogen evolution corrosion test was carried out in Hanks' solution during 192 h. The additions of 0.2 - 0.3 wt.% Ca, Y and Nd to Mg4Zn4Ga alloy promote the increasing of the corrosion rate for about two times.

Keywords: Biodegradable materials, magnesium alloys, gallium, ECAP, Hanks' solution

1. INTRODUCTION

Magnesium alloys are good candidates for using as biodegradable materials because of high biocompatibility, enough mechanical properties and acceptable biodegradation rate [1, 2]. Zinc is one of the most commonly used alloying elements in Mg due to good solid solution and precipitation strengthening [3]. At a high concentration the Zn has a neurotoxic effect and hinders bone development, but daily allowance level (15 mg) is too high versus other alloying elements [3].

Gallium also has high strengthening potential [4, 5]. The biological effect of Ga is remained an open question but some good properties are known. Gallium is effective against bone resorption and osteoporosis [6] and is also effective in the treatment of disorders associated with accelerated bone loss, including cancer-related hypercalcemia and Paget's disease [7]. Gallium decreases the corrosion rate of magnesium and does not show strong cytotoxicity [8]. Coatings with gallium had a positive effect on cell adhesion and improved the cytocompatibility of the Mg - 10 wt.% Gd and Mg - 0.8 wt.% Ca magnesium alloys [9].

The goal of this work is to investigate the microstructure, mechanical and corrosion properties of Mg - 4 wt.% Zn - 4 wt.% Ga based alloys with small additions of Ca, Y and Nd that are good candidates for using as biodegradable materials.

2. MATERIALS AND METHODS

The alloys having a base composition Mg - 4 wt.% Zn - 4 wt.% Ga (Mg4Zn4Ga) with additions of Ca, Y and Nd were investigated. The following raw materials were used for alloys preparation: magnesium (99.9 wt.% Mg), zinc (99.98 wt.% Zn), gallium (99.99 wt.% Ga) and Mg - 30 wt.% Ca, Mg - 20 wt.% Nd, Mg - 20 wt.% Y master alloys. Melt was prepared using the induction furnace in a steel crucible under cover of carnallite flux. The cylindrical ingots were obtained by a steel permanent mold casting. The chemical composition of the alloys is presented in **Table 1**. The ingots were solution heat treated at 400 °C during 75 hours in order to dissolve nonequilibrium eutectic phases and homogenize structure.

Table 1 Prepared alloys composition (wt.%)

Alloys	**Mg**	**Zn**	**Ga**	**Other**
Mg4Zn4Ga	Bal.	4.13	4.04	-
Mg4Zn4Ga0.05Ca	Bal.	3.69	3.62	0.06 Ca
Mg4Zn4Ga0.2Ca	Bal.	3.67	3.69	0.19 Ca
Mg4Zn4Ga0.3Y	Bal.	3.73	3.59	0.30 Y
Mg4Zn4Ga0.3Nd	Bal.	3.57	3.45	0.34 Nd

Cylinders with diameter of 20 mm for equal channel angular pressing (ECAP) were cut from ingots using spark cutting. The ECAP processing was carried out using a die with channel having a diameter of 20 mm and channel angle of 90°. The samples were processed for four passes in which the sample was rotated along its longitudinal axis to 90° after first pass and for 180° and 90° after second and third passes. The samples and die were preheated to 310 °C.

The alloys samples were polished for metallographic observations. The microstructure analysis and energy dispersive X-ray spectroscopy analysis (EDS) were carried out using a Tescan Vega SBH3 Scanning Electron Microscope with EDS system Oxford. The alloys chemical composition was determined by EDS analysis on alloys metallographic sections in a surface with an area of 1 mm^2. For each sample three areas were analyzed.

In vitro corrosion test was carried out on alloy samples after ECAP processing. The disks, having 18 mm diameter and 5 - 6 mm height, were spark machined and grounded. The samples surface area was approximately 8 cm^2. Samples were immersed in Hanks' solution produced by "PanEco" company (Russian Federation) at 37 °C for 192 h. Hydrogen evolution by corroding specimens was measured as a function of time and normalized to 1 cm^2 of surface area. During the corrosion test, the change of Hanks' solution pH was measured as time function using pH211 Hanna Instruments pH meter. The Hanks' solution volume was 600 ml for Mg4Zn4Ga0.3Nd and 300 ml for other alloys in order to determine the effect of solution volume on corrosion rate.

The alloy samples after ECAP processing 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**. Microstructure of Mg4Zn4Ga alloy in as-cast condition consists of magnesium solid solution dendrites (Mg) and eutectic phase. In accordance with Mg - Ga and Mg - Zn binary phase diagrams Mg_5Ga_2 and Mg_7Zn_3 can be found in Mg - 4 wt.% Ga and Mg - 4 wt.% Zn alloys microstructure [10, 11]. Using EDS analysis the Zn and Ga content in eutectic phase was determined. Its composition changed from Mg - 5 at.% Zn - 22 at.% Ga to Mg - 22 at.% Zn - 5 at.% Ga. It is expected that the eutectic consists of two phases. This phases can be denoted as $(Mg,Zn)_5Ga_2$ and $(Mg,Ga)_7Zn_3$. No information about ternary phases is found in the literature but it can also be present in alloy structure. Ca addition is accumulated in $(Mg,Zn)_5Ga_2$ and $(Mg,Ga)_7Zn_3$ eutectic phases. Y and Nd formed new eutectic phases. The Ca, Y and Nd content in (Mg) is lower than EDS determination limit.

The alloys microstructures changed significantly after the heat treatment during 75 h at 400 °C. In Mg4Zn4Ga and Mg4Zn4Ga0.05Ca alloys only small amount of spheroidized eutectic phase remained. The spherical pores are observed in alloys microstructure. The Zn and Ga content in (Mg) are almost the same as content of these elements in alloy. The bright phase on grain boundaries in Mg4Zn4Ga alloy microstructure makes possible to reveal the grains. The grain size in a heat treated Mg4Zn4Ga alloy is 69 μm, it was determined by linear intercept method. In Mg4Zn4Ga0.05Ca alloy microstructure it is the same as for Mg4Zn4Ga alloy but the grain boundaries are not visible. The diffusion pores are absent in Mg4Zn4Ga0.2Ca, Mg4Zn4Ga0.3Y and Mg4Zn4Ga0.3Nd alloys microstructures. The eutectic phase, observed on the grain boundaries of Mg4Zn4Ga0.2Ca alloy revealed the grains. The grain size of Mg4Zn4Ga0.2Ca alloy is 300 μm. In alloys with addition of Y and Nd the small eutectic particles remained in alloys structure after heat treatment. In alloys with Ca, Y and Nd addition after the heat treatment these elements are not present in the (Mg). That is the reason why the eutectic phase remains after the heat treatment.

The Mg4Zn4Ga and Mg4Zn4Ga0.3Y alloys samples are fractured during third pass and Mg4Zn4Ga0.3Nd alloy sample fractured during fourth pass of ECAP. Only Mg4Zn4Ga0.05Ca and Mg4Zn4Ga0.2Ca alloys survived after four ECAP passes. The alloys have similar microstructure after ECAP that consists of (Mg) grains and particles of bright phases that were described earlier. The particles of bright phases with size near 1 μm or smaller can be observed inside the grains and on the grain boundaries. The grain boundaries are clearly seen in alloy microstructure. This made possible to measure the grain size by the linear intercept method. The variety of a grain size can be observed in Mg4Zn4Ga and Mg4Zn4Ga0.05Ca alloys. The microstructure of Mg4Zn4Ga after ECAP processing is presented in **Figure 1**. In the upper left part of the microstructure there is the one large grain surrounded by many small grains. The size of the large and the small grains is about 150 μm and 10 μm respectively. In alloys with 0.2 - 0.3 wt.% of Ca, Y and Nd the uniform-sized grains with size in the range of 5 - 15 μm were observed.

The yield strength (YS), ultimate tensile strength (UTS) and elongation (EL) of alloys after ECAP processing is shown in **Figure 2**. The YS of Mg4Zn4Ga and alloys with Ca addition are the same and near the 165 MPa. Addition of Y and Nd reduced YS to 140 MPa. The values of UTS are within 280 - 300 MPa for all the alloys except Mg4Zn4Ga0.2Ca. The UTS of Mg4Zn4Ga0.2Ca alloy is only 255 MPa. All the alloys have the high EL that exceeded 15 %. The maximal elongation 25 - 30 % is obtained on samples of Mg4Zn4Ga0.05Ca and Mg4Zn4Ga0.3Nd alloys. The obtained results showed that addition of Ca, Y and Nd to Mg4Zn4Ga does not provide significant change of mechanical properties.

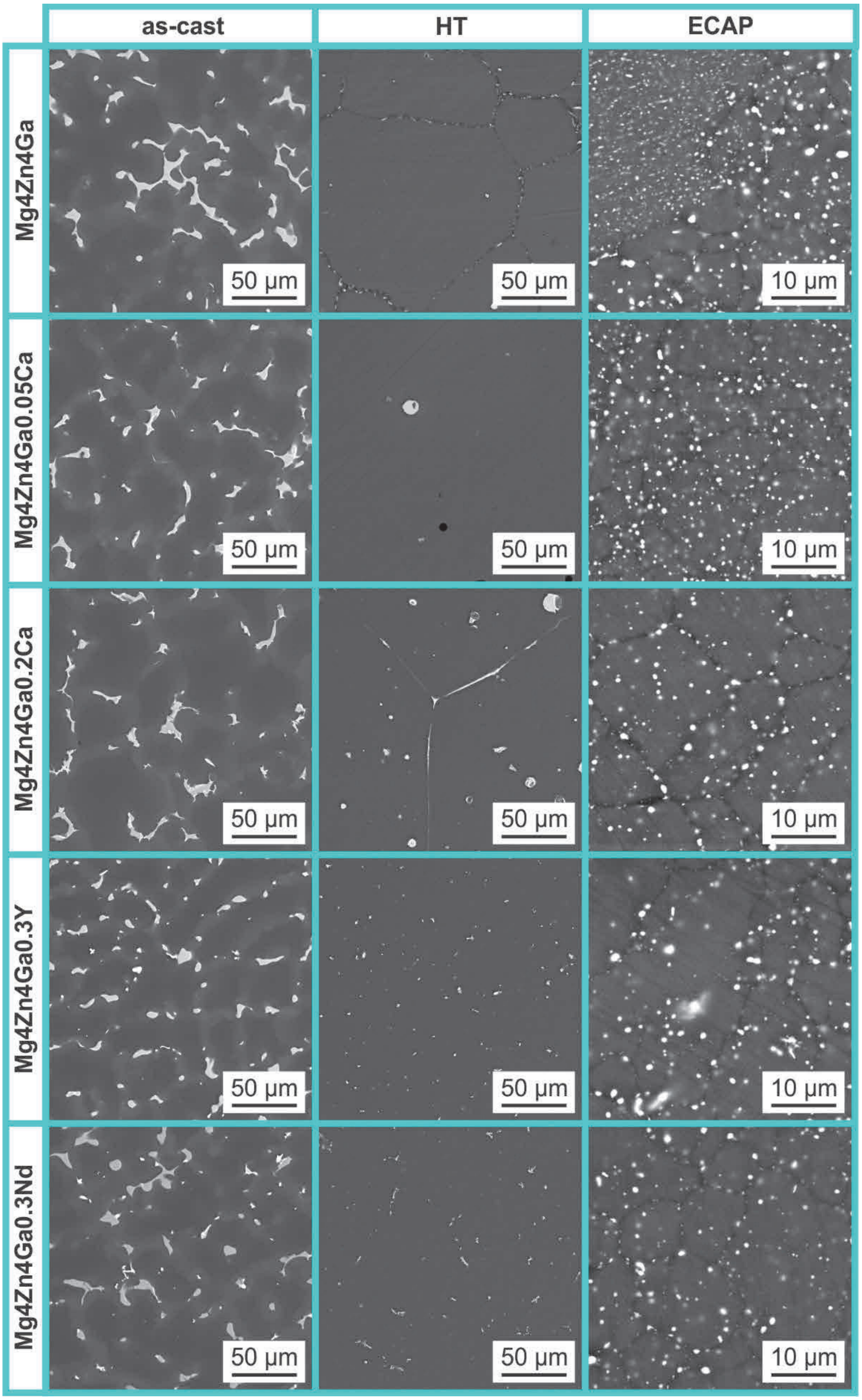

Figure 1 Microstructure of alloys in as-cast condition (at left) after solution treatment at 400 °C during 75 h (at center) and after ECAP processing (at right)

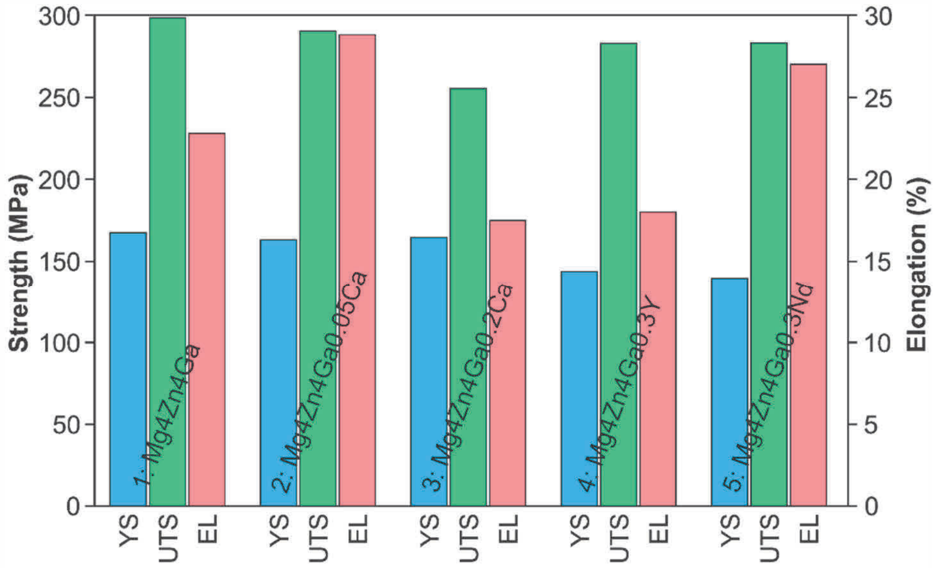

Figure 2 Mechanical properties of alloys after ECAP processing

Results of ECAP processed samples corrosion test in Hanks' solution was shown in **Figure 3**. It can be seen that lowest corrosion rate was observed for Mg4Zn4Ga0.05Ca alloy. The small addition of Ca promotes twice decreasing of evaluated hydrogen amount. The 0.2 - 0.3 wt.% additions of Ca, Nd and Y results in corrosion rate increasing and evaluated amount of hydrogen is 4 ml/cm^2 for 50 h. As a comparison the similar amount of hydrogen is evaluated from Mg4Zn4Ga alloy sample after 150 h corrosion test duration. The corrosion rate was decreased in time for all alloys except Mg4Zn4Ga0.3Nd alloy. The corrosion rate of that alloy is nearly constant due to the two times higher volume of Hanks' solution (600 ml) used. The pH value of Hanks' solution changed during corrosion test from 7.6 to 9.4.

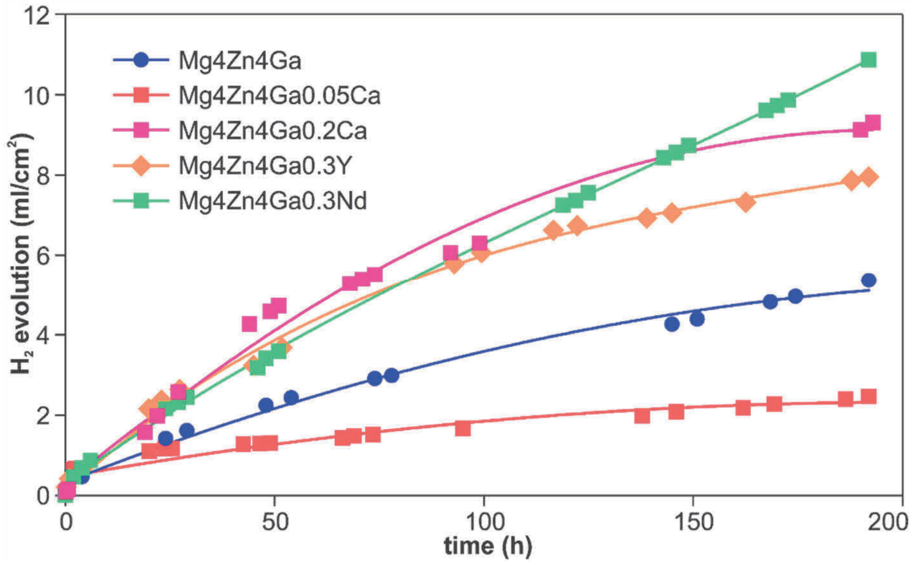

Figure 3 Hydrogen evolution during holding of alloys samples in Hanks' solution at 37 °C

4. CONCLUSION

The microstructure of Mg4Zn4Ga alloy after ECAP processing consists of large grains with size of 150 μm surrounded by small grains with size of 10 μm. The small additions of 0.2 - 0.3 wt.% of Ca, Y and Nd to Mg4Zn4Ga alloy promote the formation of small grains with sizes 5 - 15 μm. Mentioned additions have no effect on mechanical properties of Mg4Zn4Ga alloy after ECAP processing. The mechanical properties of Mg4Zn4Ga alloy are UTS 298 MPa, YS 167 MPa and El 23%. The increasing of corrosion rate of Mg4Zn4Ga alloy in Hanks' solution after 0.2 - 0.3 wt.% additions of Ca, Nd and Y is observed. The smallest corrosion rate is observed for Mg4Zn4Ga alloy with 0.05% Ca. Alloys corrosion rate are decreased with time and pH are increased.

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