Structural investigation of Mg-3Ca, Mg-3Zn-1Ca and Mg-3Zn-3Ca as cast alloys

INTRODUCTION
Magnesium alloys made of Mg-Zn-Ca system are interesting, because of possible application as bioresorbable cardiovascular stents or orthopaedic implants [1-3]. During the last ten years, rapid growth of research in the application of magnesium and its alloys as biomaterials has been observed [4-6]. Usage of magnesium based bone implants instead of those made of titanium or steel allows to avoid the removal surgery. Mg is the lightest of all structural metals with density close to those typical for cortical bone (1.75-2.1 g/cm³). Other material parameters, like Young’s modulus (~45 GPa) are also similar [3]. Moreover, Mg is considered as biocompatible and non-toxic material and has been shown to increase the rate of new bone formation – it is an important ion in the formation of the biological apatites [3]. It was reported that the adult person normally consumes about 300÷400 mg of magnesium every day and an excess of Mg²⁺ is excreted through the urine [7, 8]. Magnesium is a cofactor for many enzymes and stabilized the structures of DNA and RNA [7, 8]. It is worth noticing that calcium and zinc are also recognized as biocompatible elements [1, 9].

A lot of studies have been performed on rare elements or/and Al containing alloys [10, 11], but these additions increase the cost of possible implant, and biocompatibility of RE is doubtful. An addition of Al can influence human nerves and induces Alzheimer disease [12]. From the metallurgical point of view, alloys made of Mg-Zn-Ca system can undergo solid-solution hardening and Ca is believed to be an effective grain refiner [13-15]. In spite of possible benefits from magnesium based bone implants, there are a few important questions, which remain open up to date. There are problems with precise control of corrosion rate, which is usually very rapid and connected with hydrogen evolution. Rapid release of H₂ in a high amount may cause inflammation process or even death [16]. Thus, improvement of the corrosion resistance is a key problem for successful implant applications of Mg [2, 3, 16]. One method of influencing the process of corrosion is alloying with other elements followed by proper heat treatment. Another issue is related to understanding relation between phases existing in the material, microstructure and corrosion rate [17]. Du et al. [3] reported enhancement of ultimate tensile strength and corrosion resistance by addition of 2 Zn wt % into Mg-3Ca wt % alloy. This improvement was connected to the formation of Ca,Mg,Zn₃ phase. Bakhsheshi-Rad et al. investigated Mg-3Ca-xZn alloys and reported that addition up to 1 wt % of Zn increase the corrosion resistance whereas further addition reverses the process [2]. They concluded that presence of Mg,Ca phase is beneficial for the alloy. As suggested above, the identification of type of phases in the investigated alloys is crucial.

EXPERIMENTAL STUDY
Alloys of nominal composition presented in Table 1 have been prepared from Zn (99.999%), Ca (99.9%) and Mg (99.9%) under the argon atmosphere. Calcium has been added in a form of master alloy (Mg-33 Ca wt %). Melted alloys have been kept for 10 min at 750°C to ensure that all alloying elements have dissolved in the melt. Subsequently melted alloys have been poured into the graphite moulds. Nominal chemical compositions and Ca/Zn ratio of the investigated alloys are listed in Table 1.

All specimens for scanning electron microscopy (SEM) and X-ray diffractometer (XRD) have been prepared by standard metallographic procedures. FEI ESEM XL30 with energy dispersive X-ray (EDS) has been used to observe the microstructure of all samples. Examination of phases in the as-cast alloys has been done by XRD using Philips PW 1840 X-ray diffractometer with Co Kα radiation (λ = 1.78896 Å) and by transmission electron microscopy (TEM) using Tecnai G2 F20 (200 kV) microscope equipped with high-angle annular dark field scanning transmission electron microscopy detector (HAADF-STEM) and energy dispersive X-ray (EDS) EDAX microanalysis. TEM specimens have been prepared by twin-jet electropolishing (Tenupol-5) using a solution of 10.6 g lithium chloride LiCl, 22.32 g magnesium perchlorate Mg(ClO₄)₂, 1000 ml methanol, and 200 ml 2-butoxy-ethanol at ~40°C and 80 V. Afterwards, the oxide layer has been removed from the specimen surface using Leica EM RES101 Ion Beam Milling System. Hardness measurements have been performed using Zwick/Roell ZHU 250 hardness tester with an indenter load of 49 N (5 kGf). Ten indentations have been measured for each sample.

RESULTS AND DISCUSSION
Scanning electron microscopy (SEM)
Figure 1 shows the SEM micrographs of as-cast Mg-3Ca, Mg-3Zn-1Ca and Mg-3Ca-3Ca alloys, respectively. All alloys have revealed α-Mg dendrites surrounded by intermetallic phases. Two types of intermetallic phases: Ca,Mg,Zn and Mg,Ca have been observed in the Mg-3Zn-3Ca alloy. In the Mg-3Zn-1Ca alloy only the ternary phase has been identified. As suspected, Mg-3Ca contains only one type of phase: Mg,Ca. It is visible that Ca is an effective grain refiner for the Mg-Zn alloys and amount of intermetallic phases increases with an increase in calcium content. Similar microstructures were observed by Du et al. [3].

Figure 2 shows SEM micrograph of Mg-3Zn-3Ca alloy with higher magnification. It is clearly visible that two phases have been formed in interdendritic areas. Brighter areas represent ternary Ca,Mg,Zn phase and darker regions correspond to Mg,Ca binary phase. The identified phases are confirmed by X-ray diffraction and described in the next subsection.

Table 1. Nominal chemical composition of investigated as-cast alloys from the Mg-Zn-Ca and Mg-Ca system

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Ca/Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-3Ca</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>Mg-3Zn-1Ca</td>
<td>96</td>
<td>3</td>
</tr>
<tr>
<td>Mg-3Zn-3Ca</td>
<td>94</td>
<td>3</td>
</tr>
</tbody>
</table>
X-ray diffraction

Figure 3 shows the XRD spectra of all studied alloys. Except \(\alpha\)(Mg), hexagonal ternary phase \(\text{Ca}_2\text{Mg}_6\text{Zn}_3\) has been detected for the Mg-3Zn-1Ca alloy and Mg-3Zn-3Ca (\(\text{Ca}_2\text{Mg}_6\text{Zn}_3\) phase has hexagonal crystal structure; space group \(\text{P}6_3\text{mmc}\), with lattice parameters depending on the alloy composition [18]). It was calculated that the unit cell parameters for the ternary compound change – \(a\) from 9.912 to 9.945 Å, \(c\) from 10.351 to 10.378 Å, if compare Mg-3Zn-1Ca to Mg-3Zn-3Ca. The Mg-3Ca alloy contains only Mg\(_2\)Ca (hexagonal crystal structure; space group \(\text{P}6_3\text{mmc}\), with lattice parameters \(a = 6.239\) Å and \(c = 10.146\) Å). The same binary phase has been identified in Mg-3Zn-3Ca alloy, but with slightly changed parameters: \(a = 6.2152\) Å and \(c = 10.0699\) Å.
Transmission electron microscopy (TEM)

Figure 4a shows characteristic precipitation of Ca$_2$Mg$_6$Zn$_3$ ternary phase in the Mg-3Zn-1Ca alloy with corresponding selected area diffraction pattern taken along [1011] zone axis. EDS results have shown that the composition of this phase is as follows: 61.3 at.% Mg, 23.4 at. % Zn and 15.3 at. % Ca. Fig. 4b presents STEM-HAADF image of Ca$_2$Mg$_6$Zn$_3$ precipitation in the Mg-3Zn-3Ca alloy and chemical composition of this phase is: 66.0 at. % Mg, 19.9 at.% Zn and 14.1 at. % Ca.

Changes in the chemical composition of this ternary phase causes the change in lattice parameters and stay in a good agreement with results obtained from X-ray diffraction. Similar dependence of cell parameters and chemical composition was also observed by Zhang et al. [19] and is described in details in our previous work [18].

Hardness

Figure 5 shows hardness of Mg-3Ca, Mg-3Zn-1Ca and Mg-3Zn-3Ca alloys. The highest value 68 HV was observed for Mg-3Zn-3Ca alloy whereas hardness of alloy containing only calcium was significantly lower 49 HV.

Fig. 5. Hardness of Mg-3Ca, Mg-3Zn-1Ca and Mg-3Zn-3Ca alloys with standard deviation bars

Rys. 5. Twardość stopów: Mg-3Ca, Mg-3Zn-1Ca oraz Mg-3Zn-3Ca. Na wykresie zaznaczono odchylenie standardowe

CONCLUSIONS

1. All investigated alloys have revealed α(Mg) dendritic microstructure with intermetallic phases distributed in interdendritic spacings. The Mg$_2$Ca has been identified as the intermetallic phase in the Mg-3Ca wt % alloy. Zinc addition causes the formation of ternary Ca$_2$Mg$_6$Zn$_3$ phase and only this phase has been identified in Mg-3Zn-1Ca wt % alloy. In the Mg-3Zn-3Ca wt % alloy, apart from Ca$_2$Mg$_6$Zn$_3$ phase, the Mg$_2$Ca phase has been also identified. If Ca/Zn ratio is high enough than the precipitation of binary Mg$_2$Ca takes place.

2. Lattice parameters of Ca$_2$Mg$_6$Zn$_3$ increase with an increase in Ca content ($a = 9.912÷9.945$ Å; $c = 10.351÷10.378$ Å) if compare Mg-3Zn-1Ca with Mg-3Zn-3Ca. Reverse behaviour has been observed for binary Mg$_2$Ca phase – addition of zinc into the alloy causes decrease in the lattice parameters.

3. Alloys hardness increases with an increase in Ca content.

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REFERENCES


