Alloys of nominal composition Mg-3Zn-xCa (x = 0, 0.2, 0.5, 0.7, 1.0, 1.3) wt.% have been prepared by resistance melting and casting into graphite mould under argon atmosphere. All investigated alloys have revealed \( \alpha(Mg) \) dendritic microstructures with intermetallic phases distributed in interdendritic spacing. The Mg\(_2\)Zn\(_7\) has been identified as the main phase which coexists with \( \alpha(Mg) \) in the Mg-Zn alloy. Calcium addition causes the formation of ternary Ca\(_x\)Mg\(_y\)Zn\(_{2-x}\) hexagonal phase, denoted also as Ca\(_6\)Mg\(_3\)Zn\(_{15-x}\). The increase of Mg/Zn ratio from 0.59 in Mg-3Zn-0.2Ca wt.% alloy to 2.72 in Mg-3Zn-1.3Ca wt.% alloy in this phase is connected with an increase in the lattice parameters. The microhardness of the Ca containing alloys increases up to 67 HV (for the alloy containing 1.3 wag.% Ca) compared to the 50 HV for Mg-3Zn wt.% alloy.

**Keywords**: magnesium alloy, Mg-Zn-Ca, Ca\(_x\)Mg\(_y\)Zn\(_{2-x}\), microstructure, TEM

Stopy o składach Mg-3Zn-xCa (x = 0, 0.2, 0.5, 0.7, 1.0, 1.3) %wag. topiono w piecu oporowym w atmosferze argonu i odłano do trygu grafitowego. Wszystkie badane stopy posiadają po odłaniu mikrostrukturę dendrytyczną \( \alpha(Mg) \), z obecnością faz międzymetalicznych w przestrzeniach międzydendrytycznych. Głowiącą fazę międzymetaliczną w stopie Mg-3Zn (referencyjnym) była faza Mg\(_2\)Zn\(_7\). Dodatek Ca powoduje tworzenie się heksagonalnej fazy potrójnej Ca\(_x\)Mg\(_y\)Zn\(_{2-x}\), opisywanej również jako Ca\(_6\)Mg\(_3\)Zn\(_{15-x}\). Stosunek Mg/Zn w tej fazie zmienia się od wartości 0.59 dla stopu Mg-3Zn-0.2Ca do 2.72 dla stopu Mg-3Zn-1.3Ca, co związane jest ze zwiększaniem się parametrów komórki elementarnej. Obecność Ca w stopie powoduje wzrost mikrotwardości do 67 HV dla stopu zawierającego 1.3 wag.% Ca (w porównaniu do 50 HV dla stopu Mg-3Zn).

**1. Introduction**

Nowadays, magnesium alloys from the Mg-Zn-Ca system are in a region of interest in terms of biomaterials engineering as well as in industrial application as lightweight structure materials [1]. In particular, magnesium alloys can be used to manufacture biocompatible and bioresorbable temporary orthopedic implants due to their specific corrosion behavior and mechanical properties similar to that of human bone [2, 3]. Especially lower Young’s modulus (~45 GPa) compared to other metallic materials used for implants and the density (1.7-2.0 g/cm\(^3\)) makes the material interesting from biomedical point of view [2, 3]. Moreover Mg, Ca and Zn are considered as biocompatible elements and can be metabolized in a human body. The biocompatibility of some alloys from Mg-Zn-Ca system has been indicated by Sun et al. [4] and Zhang et al. [5]. From a metallurgical point of view the Mg-Zn-Ca system shows better precipitation hardening ability compared to Mg-Zn alloys, which causes higher hardness and creep resistance [6, 7]. Furthermore calcium is believed to be a possible grain refiner in the Mg-Zn system and enhances corrosion resistance of magnesium alloys [4, 6].

Bamberg et al. [8] have suggested that precipitation of Ca\(_6\)Mg\(_3\)Zn\(_{15-x}\) ternary phase is responsible for the age hardening response in alloys from the Mg-Zn-Ca system and the presence of CaMg\(_{2}\)Zn\(_3\) phase is disadvantageous for this process. The effect is still under investigation by many researchers. Langelier et al. [9] have recently reported that presence of CaMg\(_2\)Zn\(_3\) has no significant influence on hardness increase in the Mg-0.9Zn-2.1Ca wt.% alloy. What is interesting, they have not found ternary Ca\(_6\)Mg\(_3\)Zn\(_{15-x}\) phase in the alloy. Oh-ishi et al. [10] have studied several alloys composition with 0.5 wt.% Ca and Zn content up to 4.2 wt.% It has been found that maximum peak hardness occurs for the optimal composition: Mg-0.5Ca-1.6Zn wt.% alloy. Ca\(_3\)Mg\(_6\)Zn\(_3\) has been identified as responsible for the age-hardening process, but hardness of this alloy is not very high.

Recently, the isothermal section of Mg-Zn-Ca phase diagram at 335°C has been constructed by Zhang et al. [11, 12] using diffusion couples method. However insufficient number of samples containing less than 1 at.% Ca have been analyzed. Work of Zhang et al. [11, 12] has allowed to resolve some inconsistencies regarding crystal structure of Ca\(_3\)Mg\(_6\)Zn\(_3\) phase [10, 13-16] and the notation Ca\(_3\)Mg\(_6\)Zn\(_{15-x}\) has been proposed.

Based on the literature review, particular compositions of alloys with possible good age-hardening response and corrosion behavior have been chosen. Moreover these compositions
can help to fulfill the gap in the Mg-Zn-Ca ternary phase diagram. In order to design a successful implant with proper mechanical and corrosion characteristics or lightweight structural material all data connected with microstructure have to be known. Knowledge about types of phases in as-cast alloys from the Mg-Zn-Ca system allows to understand precipitation sequence during age-hardening treatment. Results obtained by different groups of scientists are not consistent, types of existing phases in the chosen area of isothermal section have not been established yet [11, 12]. Therefore the microstructure, chemical composition and crystal structure of phases in selected alloys from the Mg-Zn-Ca system have been systematically investigated in this work.

2. Experimental procedure

Alloys of nominal composition Mg-3Zn-xCa (x=0, 0.2, 0.5, 0.7, 1.0, 1.3) wt.% 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.%). Melt alloys have been kept for 10 min at 750°C to ensure that all alloying elements have dissolved in the melt. Subsequently melt alloys have been poured into the graphite moulds. Nominal chemical compositions and Ca/Zn ratio of the investigated alloys are listed in Table 1. In this paper all composition of the alloys are described in wt. %.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition (wt. %)</th>
<th>Composition (at. %)</th>
<th>Ca/Zn (at. %)</th>
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<tr>
<td>Mg-3Zn</td>
<td>97</td>
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<td>98.43</td>
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<td>1.0</td>
<td>98.24</td>
</tr>
<tr>
<td>Mg-3Zn-1.3Ca</td>
<td>95.7</td>
<td>1.3</td>
<td>98.05</td>
</tr>
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</table>

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

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 (EDX) has been used to observe the microstructure of all samples. Preliminary 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). Detailed studies of distribution and types of phases have been done 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 (EDX) EDAX microanalysis. TEM specimens have been prepared by twinjet electro-polishing (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 have been removed from the specimen surface using Leica EM RES101 Ion Beam Milling System. Hardness measurements have been performed using CSM Instrument with an indenter load of 1 N (102 g) and a loading time of 30s. Ten indentations have been measured for each sample.

3. Results and discussion

Fig. 1 shows the SEM micrographs of as-cast samples from the Mg-Zn-Ca system and the Mg-3Zn reference sample. All alloys have revealed α-Mg dendrites surrounded by the intermetallic phases. Dendritic microstructure, like in Fig. 1a, has been observed by Gao and Nie [17] for the Mg-8Zn wt.% as-cast alloy. Microstructure for Mg-3Zn-0.5Ca alloy (Fig. 1c) is similar to that observed by Bamberg et al. [8] for the Mg-1.9Zn-0.3Ca wt.%. However, in their case micropores have been detected. In this study, the appearance of pores has been avoided due to use of the graphite mould. It is clearly visible that microstructure becomes finer and the amount of intermetallic phases located in the interdendritic region increases with increasing Ca content in the alloy. Therefore, Ca is a possible grain refiner for the Mg-Zn system.

![Fig. 1. SEM micrographs of as-cast alloys: (a) Mg-3Zn, (b) Mg-3Zn-0.2Ca, (c) Mg-3Zn-0.5Ca, (d) Mg-3Zn-0.7Ca, (e) Mg-3Zn-1.0Ca, (f) Mg-3Zn-1.3Ca](image)

Fig. 2 shows the XRD spectra of all studied alloys. Except α(Mg), one hexagonal ternary phase Ca₂Mg₆Zn₁ has been detected for the alloys containing 0.5 wt.% of Ca or more (Ca₂Mg₆Zn₁ phase has hexagonal crystal structure; space group P6₃/mmc, with lattice parameters depending on the alloy composition [11]). Reflections of the ternary phase shift towards lower angles with increasing Ca content. It was calculated that the unit cell parameters for the ternary compound (Fig. 2) are: from 9.725 to 9.912 Å: c: from 10.148 to 10.352 Å The same phenomenon has been observed by Zhang et al. [11, 12] but for different alloy compositions. New notation Ca₁₅Mg₂Zn₁₅ has been proposed [11], which seems to be reasonable due to extensive solubility range of this compound. Other phases could not be identified in investigated alloys because of low sensitivity of the method, even Ca₂Mg₆Zn₁ phase begins to be detectable in the Mg-3Zn-0.5Ca alloy. Therefore further investigation using transmission electron microscopy has been done.
Fig. 2. XRD patterns of investigated alloys from the Mg-Zn-Ca system

Fig. 3a shows STEM-HAADF image of the Mg-3Zn alloy presented particle composed of zinc-rich regions (bright areas) and α-Mg solid solution located between them (dark areas with contrast similar as surrounding matrix). EDX microanalysis has shown that the bright areas contain 35.1 at.% of Mg and 64.9 at.% of Zn, which corresponds to the Mg$_4$Zn$_7$ phase. Selected area diffraction pattern (SADP) obtained from the part of Zn rich phase (Fig. 3c) confirms the Mg$_4$Zn$_7$ phase (zone axis [101]). The Mg$_4$Zn$_7$ phase has a base-centered monoclinic structure (space group C$\overline{2}$m, lattice parameters: $a = 25.96$ Å, $b = c = 5.24$ Å, $\beta = 102.5^\circ$) [17].

Fig. 3. Mg-3Zn alloy: (a) STEM-HAADF image; (b) TEM bright field image of the magnified part of the particle shown in (a) and (c) corresponding selected area diffraction pattern – [101] zone axis of the Mg$_4$Zn$_7$ phase

Apart from the magnesium solid solution, ternary Ca$_2$Mg$_6$Zn$_3$ phase is the main intermetallic phase present in calcium containing alloys (detected by XRD for alloys with higher Ca content). This ternary phase coexists with the binary MgZn phase in the Mg-3Zn-0.2Ca alloy. Fig. 4a shows the TEM microstructure of the particle consisting of both phases. This has been confirmed by the results of EDX microanalysis: 51.1 at.% Mg, 46.9 at.% Zn, 2 at.% Ca (MgZn) and 36.6 at.% Mg, 49.6 at.% Zn, 14.2 at.% Ca (Ca$_2$Mg$_6$Zn$_3$). Diffraction patterns presented in Fig. 4b and 4c correspond to Ca$_2$Mg$_6$Zn$_3$ phase (zone axis [0001]) and MgZn phase (zone axis [12$\bar{1}$9]), respectively. The MgZn phase has been identified by Khan [18] as a rombohedral crystal structure and expressed in the hexagonal coordinates, with $a = 25.69$ Å and $c = 18.104$ Å.

Fig. 4. (a) TEM bright field image of the Mg-3Zn-0.2Ca alloy and (b, c) selected area diffraction patterns for respective phases

For alloys with higher than 0.2 wt.% Ca content only ternary Ca$_2$Mg$_6$Zn$_3$ phase coexist with α(Mg) and no trace of CaMg$_2$ binary phase has been found. The binary CaMg$_2$ has been observed by Bamberg et al. [8] and Zhang et al. [11, 12] for similar alloys composition. In Fig. 5 and Fig. 6, exemplary TEM micrographs of the Mg-3Zn-0.5Ca and the Mg-3Zn-1.3Ca alloys are presented, respectively. Figure 5a shows eutectic Ca$_2$Mg$_6$Zn$_3$ + α(Mg) located at the grain boundary triple junction, while in the Fig. 5c the interdendritic precipitations of Ca$_2$Mg$_6$Zn$_3$ ternary phase are visible. For both cases the Ca$_2$Mg$_6$Zn$_3$ phase has been identified by SADPs, taken along [71$89\overline{1}$] zone axis (Fig. 5b) and along [1011] zone axis (Fig. 5d). EDX microanalysis results have shown that the compositions of Ca$_2$Mg$_6$Zn$_3$ phase are: 57.5 at.% Mg, 29.5 at.% Zn, 13.0 at.% Ca and 54.6 at.% Mg, 33.2 at.% Zn, 12.2 at.% Ca for areas shown in Fig. 5a and Fig. 5c, respectively. In the case of the Ca$_2$Mg$_6$Zn$_3$ phase which is the part of eutectic (Fig. 5a), Mg content in Ca$_2$Mg$_6$Zn$_3$ phase may be overestimated because of the neighborhood of the α-Mg.

Fig. 5. (a, c) TEM bright field images of the Mg-3Zn-0.5Ca alloy and (b, d) corresponding selected area diffraction patterns taken from presented particles

Fig. 6a shows the precipitation of Ca$_2$Mg$_6$Zn$_3$ phase in the Mg-3Zn-1.3 alloy. The presence of this phase has been confirmed by SADP taken along [T2$\overline{7}$0] zone axis (Fig. 6b).
The composition of this phase in Mg-3Zn-1.3Ca % wt.% alloy is: 60.9 at.% Mg, 26.0 at.% Zn and 13.1 at.% Ca.

EDX microanalysis has shown that the composition of the Ca$_2$Mg$_6$Zn$_3$ phase is strongly dependent on the composition of the alloy. Therefore several measurements of chemical composition of Ca$_2$Mg$_6$Zn$_3$ (for particles lying on the foil edge in order to avoid the influence of the matrix) have been made by EDX. The average value of the obtained results of phase composition, as well as Mg/Zn ratio (in at%) is presented in Table 2. The Mg/Zn ratio in the ternary phase has increased from 0.59 for Mg-3Zn-0.2Ca alloy to 2.72 for Mg-3Zn-1.3Ca alloy, while the Ca content remains at the same level. Similar phenomenon has been recently observed by Zhang et al. [11, 12] however in their case the Zn content in alloys has not been fixed. Therefore, due to chosen composition of alloys, it is possible to suggest that addition of Ca to the Mg-Zn system changes the solubility of Zn in Mg. With increasing Ca content in the alloy the atomic fraction of Zn in the ternary phase has been lowered from 54.1 at.% to 22.8 at.%, whereas Mg atomic fraction has increased from 31.8 at.% up to 62.0 at.%.

### TABLE 2

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition (at %)</th>
<th>Mg</th>
<th>Zn</th>
<th>Ca</th>
<th>Mg/Zn</th>
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<td>14.8</td>
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<td>1.68</td>
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<tr>
<td>Mg-3Zn-1.3Ca</td>
<td>62.0</td>
<td>22.8</td>
<td>15.2</td>
<td></td>
<td>2.72</td>
</tr>
</tbody>
</table>

Fig. 7 shows the results of microhardness measurements of as-cast alloys. The microhardness has increased with Ca addition compared to the Mg-3Zn alloy, from about 50 HV to the 67 HV for Mg-3Zn-1.3Ca alloy. The change of microhardness can be explained in relation to the formation of Ca$_2$Mg$_6$Zn$_3$ hexagonal phase and the increased amount of this phase with increasing Ca content. However, the increase is not substantial when comparing Mg-3Zn-0.2Ca to Mg-3Zn-1.3Ca alloy. Nevertheless, the change of microhardness is noticeable, what gives high expectation regarding age-hardening of the samples.

### 4. Conclusions

1. Six alloys of nominal composition Mg-3Zn-xCa (x = 0, 0.2, 0.5, 0.7, 1.0, 1.3) wt.% have been melt in resistance furnace under protective argon atmosphere using graphite mould.
2. All investigated alloys have revealed $\alpha$(Mg) dendritic microstructures with intermetallic phases distributed in interdendritic spacing. The Mg$_4$Zn$_7$ has been identified as the main intermetallic phase in the Mg-3Zn wt.% alloy. Calcium addition causes the formation of ternary Ca$_2$Mg$_6$Zn$_3$ phase. In the Mg-3Zn-0.2Ca wt.% alloy, apart from Ca$_2$Mg$_6$Zn$_3$ phase, the MgZn phase has been also identified.
3. Mg/Zn ratio in the Ca$_2$Mg$_6$Zn$_3$ phase has increased from 0.59 for Mg-3Zn-0.2Ca wt.% alloy to 2.72 for Mg-3Zn-1.3Ca wt.% alloy. Lattice parameters increase with increasing Ca content ($a = 9.725 - 9.912$ Å, $c = 10.148 - 10.352$ Å). It suggests that Ca addition to the Mg-Zn system changes the solubility of Zn in Mg.
4. Microhardness of Ca containing alloys increases to about 67 HV compared to 50 HV for Mg-3Zn wt.% alloy due to the formation of Ca$_2$Mg$_6$Zn$_3$.

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