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**Citation style:** Lesz Sabina, Hrapkowicz Bartłomiej, Gołombek Klaudiusz, Karolus Małgorzata, Janiak Patrycja. (2021). Synthesis of Mg-based alloys with a rare-earth element addition by mechanical alloying. "Bulletin of the Polish Academy of Sciences. Technical Sciences" (2021, nr 0, s. 1-6), DOI:10.24425/bpasts.2021.DOI

BULLETIN OF THE POLISH ACADEMY OF SCIENCES
TECHNICAL SCIENCES, Vol. XX, No. Y, 2021
DOI:10.24425/bpasts.2021.DOI

# Synthesis of Mg-based alloys with a rare-earth element addition by mechanical alloying

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**Abstract** Magnesium-based alloys are widely used in the construction of the automotive, aviation and medical industries. There are many parameters that can be modified during the synthesis in order to obtain an alloy with the desired microstructure and advantageous properties. Modifications to the chemical composition and parameters of the synthesis process are of key importance. In this work, Mg-based alloy with a rare-earth element addition was synthesized by mechanical alloying (MA). The aim of this work was to study the effect of milling times on Mg based alloy with a rare-earth addition on the structure and microhardness. A powder mixture of pure elements was milled in a SPEX 8000D high energy shaker ball mill under an argon atmosphere using a stainless steel container and balls. The sample was mechanically alloyed at milling times: 3,5, 8 and 13 h with 0.5 h interruptions. The microstructure and hardness of samples were investigated. The Mg-based powder alloy was examined by an X-ray diffraction (XRD), scanning electron microscopy (SEM) and a Vickers microhardness test. The results showed that the microhardness of the sample milled for 13 h was higher than that of milling time of 3, 5 and 8 h.

**Key words:** mechanical alloying; magnesium; rare-earth element; ytterbium

## 1. INTRODUCTION

Nowadays, medicine is characterized by dynamic developments – yesterday's innovations in treatment will be outdated tomorrow. Due to the increasing emphasis placed on the improvement of patients comfort and life quality, modern implantology is facing far greater challenges than ever before. Thus in the wake of growing expectations, material science has to rise to the occasion and constantly deliver advanced materials, with unique properties and unusual applications [1]–[11]. From that point of view, particularly interesting are those biomaterials, which are as much non-intrusive for the human body homeostasis as possible. The ideal biomaterial model, initially assuming total corrosion resistance, has evolved under the influence of increasing popularity of biodegradable materials [12], [13]. Hence, there is a growing demand for materials, whose properties include decomposition lacking toxic effect not only on the internal environment of living organisms, but more importantly, they can present a beneficial therapeutic impact on surrounding tissues [2], [3].

Among well-known bioinert conventionally used metallic materials, including stainless steels, Co-Cr and Ti based alloys [4], materials composing of elements already existing in the human body have attracted a considerable attention [5], [6]. According to Staiger et al. [7] magnesium in addition to being an indispensable cofactor of key enzymes for metabolism, as well as a natural component of bone is completely non-toxic to the body and innoxiously excreted in the urine. Magnesium and its lightweight alloys are particularly interesting in biomedical applications owing to their abovementioned good biodegradability and promising mechanical and physical properties [8], [14]. Elastic modulus, compressive yield strength and density are comparable to natural bone, thereby reducing the risk of osteopenia and avoiding osteolysis [1], [5], [15]. However, the fundamental issue of application crystalline magnesium-based implants is their poor corrosion resistance compared to the fast formation of hydrogen cavities around implant [16]–[19]. Therefore, it may imply difficult in healing of the damaged tissues and, as a consequence, leading to a reoperation to remove the faulty implant [20]. Moreover, due to nature of a crystal structure, solid solutions always have limited solubility of the solute, which makes it difficult to add other elements to improve the alloy. It is necessary to apply novel processing techniques and parameters which make it possible to obtain an amorphous structure. Amorphous bulk metallic glasses are well-known for their homogeneous atomic structure, which allow for dissolution of many elements, even in large concentration [8], [21]. Therefore Löffler et al. [22] proven, that addition of zinc as alloying element, above threshold of 28% contribution, significantly increases corrosion resistance and reduces activity of hydrogen cavities formations. As claimed by Byrne et al. [23] amorphous magnesium-based alloys presented a decreasing corrosion rate which directly affects the reduced hydrogen evolution, permeation and a lower tendency to form hydrogen cavities. It is reported, that the improved corrosion resistance is justified by the absence of

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defects in the amorphous structure, e.g. grain boundaries [15], [24]. The corrosion resistance can be improved by Ca addition to Mg alloys [25]. For example, AZ91Ca alloy exhibited a five-fold increase in the surface film resistance than AZ91 alloy [26]. Wang et al. [27] demonstrated that the biodegradation rate of an AZ31 alloy can be significantly reduced by grain refinement produced by mechanical processing. Guangyin et al. [28] declared that addition of calcium to Mg-based alloys efficiently reduces grain size, hence its presence in the alloy is beneficial.

There are several techniques in which bulk metallic glasses can be produced, but undoubtedly mechanical alloying has attracted significant attention in recent reports [8], [29], [30]. It is a solid state powder preparation method, based on repeatedly flattering, cold-welding, fracturing and rewelding a powder particles during dry or wet high-energy milling process, often in special atmospheres. Interaction occurs by the way of collisions between powdered particles, ball and container wall thus homogenization takes place. As a result, extremely finely ground powder (size of a grain below 1μm) is obtained [31], [32]. However there is a major disadvantage of this method in context of magnesium-based alloys, since obtained alloys are characterized by significant brittleness. Previous studies indicate, that alloying with rare-earth elements to improve the mechanical properties, can be a promising method [29], [33], [34]. Ytterbium as a rare-earth element is fully biocompatible and well-known to increase the glass-forming ability and used to thermally stabilize the alloy [24]. According to Yu et al. [21] researches it is confirmed, that adding ytterbium to the magnesium-based alloys significantly enhanced its ductility. Moreover, Liang et al. [29] reported, that compressive strength of Mg-Zn-Ca alloys after ytterbium addition has increased. Recent scientific reports suggest that ytterbium dopants in the bone structures are exhibited as novel strategy in the bone defect treatment [35].

## 2. MATERIALS AND METHODS

**2.1. Materials.** For the fabrication of sample, the high purity elements (> 99.5%) Mg, Zn, Ca and Yb, were mechanically alloyed in a dual high-energy ball mill (SPEX 8000D). Element composition of the powders is shown in Table 1. Hardened steel vial and balls were the milling media, and the ball to powder weight ratio was 10:1 [3], [8], [36]. We conducted mechanical alloying (MA) in an argon atmosphere, for a different duration of 3, 5, 8 and 13 h.

Table 1
Element composition of the Mg-Zn-Ca-Yb powders

| Element | Mg | Zn | Ca | Yb |
|---|---|---|---|---|
| at. % | 62.00 | 33.00 | 4.00 | 1.00 |
| wt. % | 37.69 | 53.97 | 4.01 | 4.33 |

**2.2. Methods.** The constituent phases of the mechanically alloyed powders were examined by the X-ray diffraction (XRD) technique (PANalytical Empyrean Diffractometer, X-ray Cu radiation $\lambda_{K\alpha}$=1.5418 Å) was analyzed. The lattice strain, lattice parameter, and crystallite size from the spectra were estimated by use the Rietveld refinement integrated with the High Score Plus PANalytical software [37]. Phase analysis were performed with ICDD PDF4+ data base.

The powder morphology in a scanning electron microscope (SEM, Zeiss SUPRA 35) was studied. The energy-dispersive spectrometer EDS (Trident XM4 EDS with 20 kV of accelerating voltage) analysis was carried out on the samples after 3, 5, 8 and 13 h of milling time. Particle size analysis using ImageJ Software was done. Chemical analysis was performed on the metallurgical specimen. The metallurgical specimen were ground and polished to following standard procedure. Accuracy of the main and major element in wt.% are 2 % and 4%, respectively and for a minor and trace elements are in a range of 10-20 % and 50-100%, respectively.

For the determination of particle size distribution (PSD) of powders laser particle size measuring instrument (Fritsch Analyssette 22 MicroTec+ ) was used. The samples powder are added to a closed circuit filled with an appropriate liquid. Therefore, wet dispersion analysis was used. In this case samples were measured in ethyl alcohol as a dispersant. The characteristic median diameter ($d_{50}$) was determined.

The microhardness tests were carried out on polished samples using a Vickers hardness tester (Future-Tech FM700) with a a load 50 grams of force applied for 15 second. At least 5 measurements under the same condition were conducted on each sample, and the average value was used as the microhardness (HV).

## 3. RESULTS AND DISCUSSION

The XRD patterns of the Mg-Zn-Ca-Yb powders, mechanically alloyed in different milling times: 3, 5, 8 and 13 h are presented in Fig. 1. The XRD patterns revealed the presence of a phase having a hexagonal close-packed (HCP) crystal structure Mg (solid state solution) and $MgZn_2$, trace of $Ca_5Zn_3$ and $CaMg_2$ phases and the presence of unreacted Zn and Yb precursors. The $MgZn_2$ phases characteristic peaks are shown after the milling process due to the mechanical alloying processes between Mg and Zn. The original sharp diffraction lines of Mg gradually become broader and their intensity decreases with milling time. After 13 hours of milling time, there is observed relaxation of main phases structure and increasing of their crystallite size. The structural analysis results obtained for studied materials is presented in Table 2.

Fig. 2 compares the scanning electron microscopy (SEM) images of the powders mechanically alloyed in different milling times: 3, 5, 8 and 13 h.

The shape and morphology of the powders are similar to one another and were irregular owing to repeated cold-welding and fracturing during MA [3], [8], [36]. The average particle size was ~57, 51 and 36 μm, after milling time 3, 5 and 8 h, respectively. The results of SEM analysis for the samples milled for 13h (Fig. 2d) reveal that the homogeneous powders are formed with fine particle sizes about 18 μm.

The XRD (Fig. 1) and SEM (Fig. 2) analysis revealed Mg-Zn-Ca-Yb powders mechanically alloyed in an argon atmosphere were micron-sized powders constituting a nanocrystalline Mg-based solid state solution and $MgZn_2$ phases.

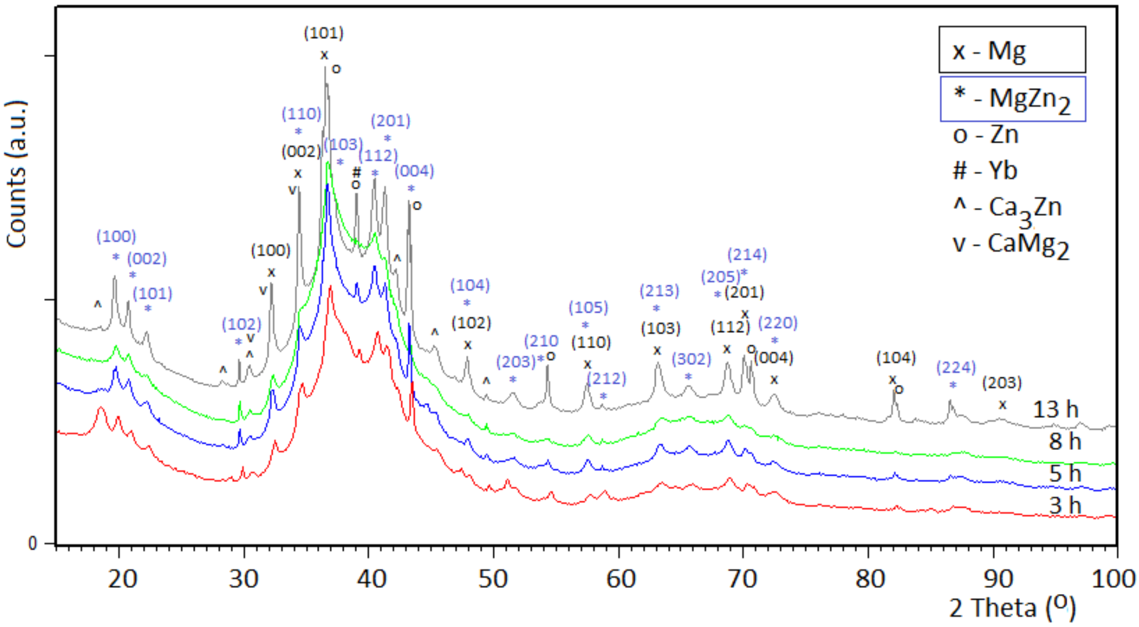

Fig. 1. X-ray diffraction patterns of the Mg-Zn-Ca-Yb powders milled for 3, 5, 8 and 13 h

Table2

Crystallite size and changes of unit cell parameters of the main phases preset in alloys after different milling time: solid state solution based on hexagonal Mg and intermetallic $MgZn_2$ phase.

| Sample (milling time) | Mg(Zn,Yb,Ca) |  |  |  | $MgZn_2$ |  |  |  |
|---|---|---|---|---|---|---|---|---|
|  | Theoretical<br>(ICDD PDF4+ card: 04-015-0486) | Refined (RR)<br>a/c [Å] | Crystallite size<br>D [Å] | Lattice strain<br>η [%] | Theoretical<br>(ICDD PDF4+ card: 04-008-7744) | Refined (RR)<br>a/c [Å] | Crystallite size<br>D [Å] | Lattice strain<br>η [%] |
| 3 | a = 3.2110<br>c = 5.2130<br>Space Group: $P6_3/mmc$<br>Crystallographic System: hexagonal | 3.2012(4)<br>5.1131(3) | 400 | 1.17 | a = 5.2210<br>c = 8.5670<br>Space Group: $P6_3/mmc$<br>Crystallographic System: hexagonal | 5.4026(9)<br>8.3412(5) | 300 | 0.37 |
| 5 |  | 3.2022(2)<br>5.1311(8) | 350 | 1.17 |  | 5.2949(9)<br>8.7643(1) | 270 | 0.37 |
| 8 |  | 3.1941(7)<br>5.0964(3) | 290 | 0.37 |  | 5.3466(7)<br>8.6679(1) | 210 | 0.06 |
| 13 |  | 3.2019(2)<br>5.2009(7) | 370 | 0.43 |  | 5.3015(9)<br>8.8776(4) | 320 | 0.05 |

Fig. 3 shows as a measured example of the cumulative curve for samples milled for 3, 5, 8 and 13 h. The diameters ($d_{10}$, $d_{50}$, $d_{90}$) determined the various characteristic fractions of powders within PSD and are presented in Table 3. All of the results were presented as the mean ± standard deviation (SD). In the initial stage of mechanical alloying (MA) process, the PSD (particle size distribution) is characterized by two peaks (Fig. 3a, b) and this is explained by the fact that the investigated powders are a mixture of particles with a largely differentiated size. This fact might be related to presence of two different main phases: Mg-based solid state solution and $MgZn_2$. Extending the milling time to 8 hours resulted in the distribution curve. It is characterized as an asymmetric deviation (Fig. 3c) in the next stage of MA. A high fraction of large particles is formed as a result of multiple welding (Fig. 3c). The asymmetry is far less and this is related to the cracking of large particles described earlier. In the last stage, a symmetric, relatively narrow distribution curve implies that the process has reached the set condition, showing the state of balance between the mechanisms of joining and fragmentation (Fig. 3d).

Each hardness value was the average of five measurements for every sample and is shown in Table 4. In Fig. 4 the influence of milling time on median diameters ($d_{50}$) of particles and average microhardness value was presented. Fig. 4 shows the average microhardness value and median diameter ($d_{50}$) for all samples.

Table 3

The characteristic diameters ($d_{10}$, $d_{50}$, $d_{90}$) of various fractions of powders. Results for samples milled for 3, 5, 8 and 13h and accuracy

| **Sample** | **Characteristic diameters (μm)** |  |  |
|---|---|---|---|
|  | **$d_{10}$** | **$d_{50}$** | **$d_{90}$** |
| 3 h | 13 ± 1.1 | 66 ± 4.5 | 163 ± 22.1 |
| 5 h | 11 ± 1.3 | 56 ± 5.5 | 106 ± 7.6 |
| 8 h | 12 ± 0.9 | 43 ± 5.1 | 103 ± 11.5 |
| 13 h | 6.5 ± 0.1 | 20 ± 0.5 | 41 ± 1.9 |

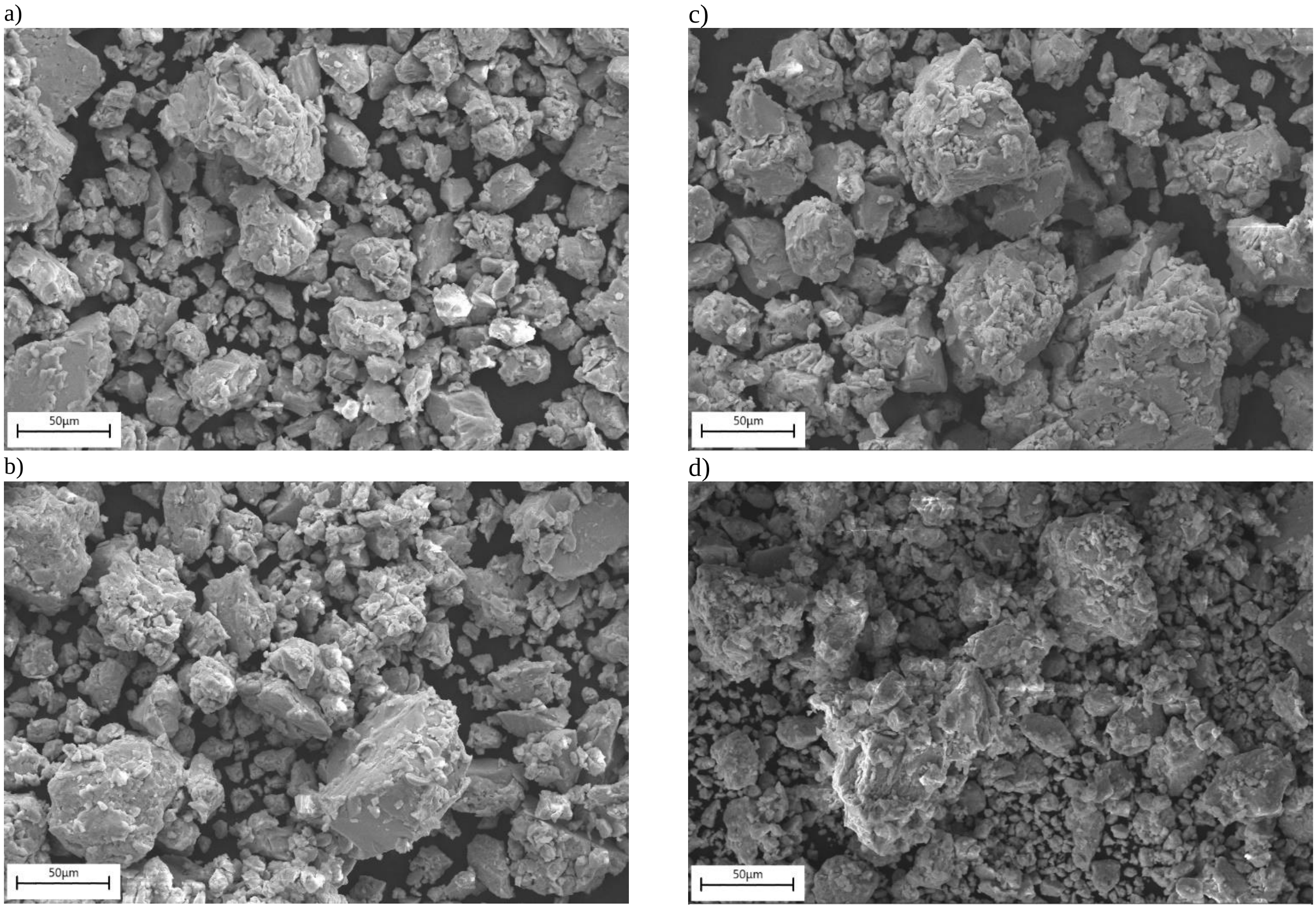

Fig. 2. SEM images of the Mg-Zn-Ca-Yb powders milled for 3, 5, 8 and 13 h

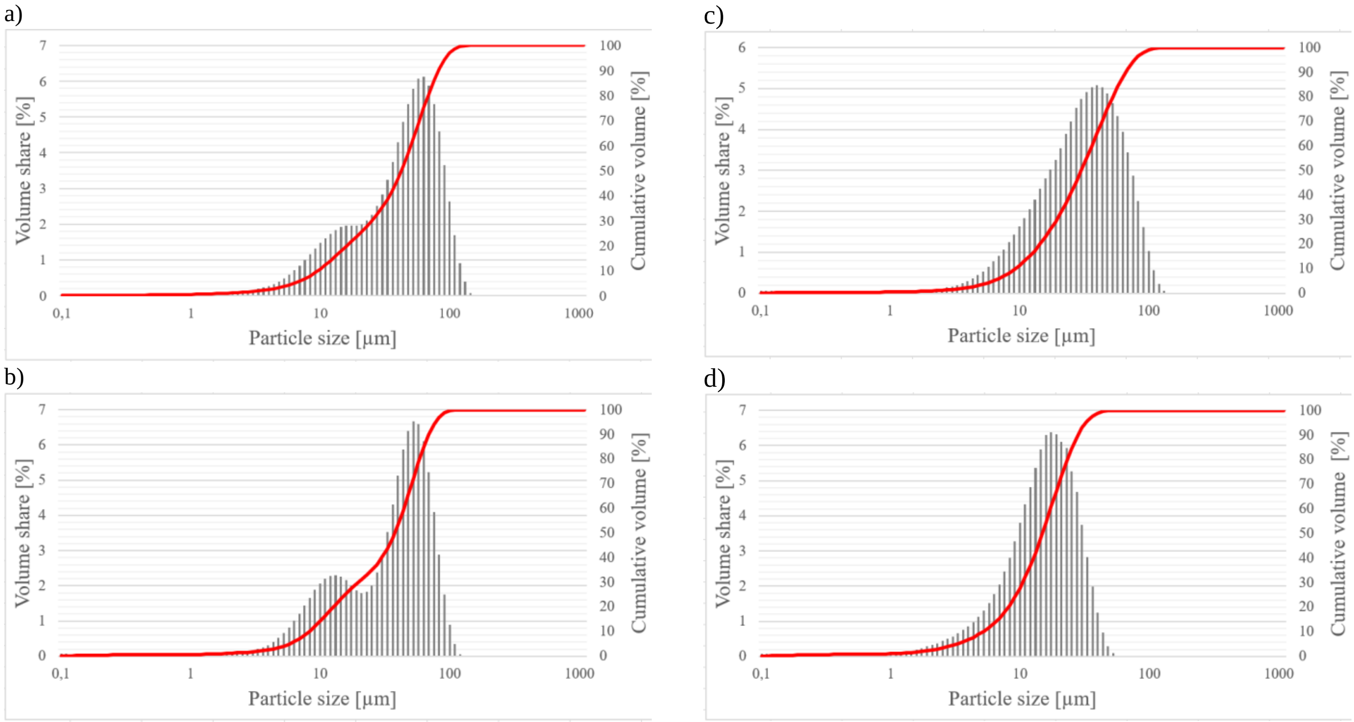

Fig. 3. The cumulative curve for samples Mg-Zn-Ca-Yb milled for 3 (a), 5 (b), 8 (c) and 13 h (d)

Table 4
Hardness value with accuracy for samples milled for 3, 5, 8 and 13 h

| **Test numer** | Microhardness **(HV 0.05) of samples milled for** | | | |
|---|---|---|---|---|
| | **3h** | **5h** | **8h** | **13h** |
| 1 | 210 | 244 | 263 | 305 |
| 2 | 316 | 221 | 246 | 290 |
| 3 | 309 | 261 | 242 | 322 |
| 4 | 326 | 319 | 306 | 336 |
| 5 | 229 | 266 | 306 | 309 |
| Average: | **278 ± 48** | **262 ± 32** | **264 ± 28** | **312 ± 15** |

Based on the diagram (Fig. 4, Table 4), the highest value of microhardness was found from the sample that was milling for 13 h (312 ± 15 HV), meanwhile the lowest value was from a sample milled for 5 h (262 ± 32 HV). The sample milled for 8 h had a similar value of microhardness (264±28). The sample milled for 3 h had value of microhardness 278±48 HV.

In the first stage of the MA process a wide hardness dispersion occurs (Table 4, Fig. 4). The particle sizes are both smaller and bigger (Fig. 3a) because some of the powder particles are trapped between the grinding balls and show strong deformation while the others are intact [8], [38], [39]. The saturation of hardness (Table 4, Fig. 4) after 13 h milling time is related to the narrow dispersion of particle sizes occurring in the last stage of MA (Fig. 3d).

The tested chemical compositions of these samples by EDS are given in Table 5. The measured chemical compositions are a little different from nominal ones, which are likely due to the oxidation of Mg during prepare of sample to SEM study.

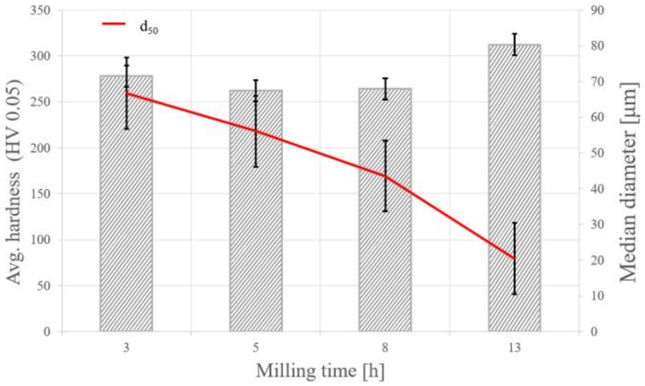

Fig. 4. Effect of milling time on microhardness (HV) and median diameter ($d_{50}$) determined for each powders

Table 5
Chemical composition of the samples. EDS (Energy-Dispersive Spectroscopy) results for sample milled for 3, 5, 8 and 13 h, respectively. Accuracy of the main elements is about 4 wt. % and minor and trace elements is in a range of 20-50 wt.%.

| Sample | at.% | | | | | wt.% | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| (milling time) | Mg | Zn | Ca | Yb | O | Mg | Zn | Ca | Yb | O |
| 3 | 61.7 | 29.2 | 4.4 | 1.2 | 3.5 | 39.3 | 50.0 | 4.6 | 4.5 | 1.6 |
| 5 | 61.4 | 28.7 | 5.6 | 1.1 | 3.2 | 39.0 | 48.9 | 5.9 | 4.9 | 1.3 |
| 8 | 62.9 | 29.7 | 3.5 | 1.2 | 2.7 | 39.7 | 50.3 | 3.6 | 5.2 | 1.2 |
| 13 | 61.9 | 25.4 | 7.4 | 1.8 | 3.5 | 40.0 | 44.6 | 7.8 | 5.9 | 1.7 |

## 4. CONCLUSIONS

The aim of this work is the synthesis of Mg-based alloys with a rare-earth element (ytterbium) addition by mechanical alloying to study the effect of milling times on the structure, morphology and microhardness.

The XRD diffraction pattern analysis showed that the milling process (gradually for 3, 5 and 8 hours) leads to formation two main nanocrystalline phases: α-Mg solid state solution and intermetallic $MgZn_2$ phase. The crystallite size of both phases are in a range of 200 – 400 Å.

The compositional homogeneity of the alloys remained consistent with the intended chemical composition.

The alloy milled at 13 hours of milling time provided the highest value of microhardness which was 312 HV. The saturation of hardness is related to the narrow dispersion of particle sizes ( ($d_{10}$= 6.5, $d_{90}$=41 μm) occurring in the last stage of MA. The particle sizes of the powders decreased with increasing milling time. The values of the median diameter ($d_{50}$) were calculated 66, 56, 43 and 20 μm for Mg-Zn-Ca-Yb after 3, 5, 8 and 13 h milling time, respectively.

## ACKNOWLEDGEMENTS

This research was funded by the National Science Center, Poland, grant number 2017/27/B/ST8/02927.

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