MAGNESIUM-ZINC ALLOY PREPARED BY MECHANICAL ALLOYING AND SPARK PLASMA SINTERING

Michaela FOUSOVÁ, Jaroslav ČAPEK, Dalibor VOJTĚCH

Department of Metals and Corrosion Engineering, Institute of Chemical Technology, Prague, Prague, Czech Republic, EU, fousovam@vscht.cz

Abstract

Mechanical alloying has been becoming widely used method for preparation of metallic materials. Its advantage lies in the possibility of obtaining amorphous or nanostructured material. However, there are problems connected with the compacting of prepared powder materials, during which coarsening of the microstructure occurs. Spark plasma sintering (SPS) may be a potential solution. It is a very fast method preventing grain coarsening and maintaining the structure very fine which leads to high mechanical properties. We used combination of these two methods to prepare Mg-Zn alloy containing 50 wt.% of zinc. Powders of pure magnesium and zinc were milled in a planetary ball mill for different times. One selected sample was subsequently compacted by SPS. Microstructure, phase composition, short-term thermal stability and hardness were examined in detail. After 8 hours of milling, the powder consisted of very fine and homogeneously distributed Mg and metastable Mg_7Zn_3 phases. During the SPS compacting Mg_7Zn_3 phase decomposed into new phases Mg, MgZn, $MgZn_2$ and Mg_2Zn_{11}. Short-term annealing did not show any differences in the phase composition. With rising annealing temperature hardness of the compacted sample (HV5 = 260) regularly decreased.

Keywords: Mg-Zn alloy, mechanical alloying, spark plasma sintering.

1. INTRODUCTION

In recent years, nanostructured and amorphous metallic materials have been intensively investigated. In comparison with crystalline materials, they possess enhanced mechanical properties and higher corrosion resistance due to the fact that their microstructure is chemically homogeneous containing no phases with different corrosion potentials. Amorphous and nanostructured metallic materials are usually fabricated by rapid solidification methods, such as atomization and melt spinning, or by mechanical alloying. Using of these methods also allows obtaining metastable phases, which often have interesting properties and cannot be obtained by conventional methods. If the metallic system possesses good “Glass-forming ability” (GFA), amorphous metallic structures, called metallic glasses, are formed by the above mentioned methods [1-3].

The disadvantage of commonly used solidification methods consists in product contamination due to high reactivity of the melt with oxygen and nitrogen traces in the atmosphere. In the case of the melt spinning method, inhomogeneity of prepared ribbons has been also described in an available literature [4]. On the other hand, mechanical alloying can achieve similar or even better results and minimizes contamination risks [5]. Mechanical alloying is a metallurgical powder processing technique used to create alloyed metals from elemental and pre-alloy powders. This two part process is accomplished by crushing the base materials in a ball mill into a fine powder form, followed by cold welding. Cold welding involves placing the elemental powders together under an extreme pressure, under a vacuum or a protective atmosphere. They are then heated by crushing to high temperatures at which sintering occurs and molecular bonds are formed. These conditions enable to weld the metal powder together without the need to melt it. The products are usually sharp-edged powders, whose inner structure is amorphous or nanostructured with large amount of dislocations [6, 7].

The semi-products of rapid solidification methods or mechanical alloying in the form of ribbons or powders have to be compacted into bulk objects for application as structural materials [7, 8]. However, conventional

compaction methods are problematic because they need to be long-term to achieve sufficient cohesiveness between powder particles. Such long-term sintering may cause undesirable grain coarsening and decomposition of amorphous and metastable phases. Recently, spark plasma sintering (SPS) is being intensively investigated as a suitable method for the preparation of nanostructured bulk materials, because compaction is usually accomplished in several minutes, which minimizes the above mentioned risks [9].

One of the metallic systems belonging between the GFA alloys are systems based on magnesium and zinc binary system containing about 28 at.% of zinc. In the amorphous state, they are considered as promising materials for production of biodegradable implants. Moreover, materials on similar base may find use in automotive, aircraft and aerospace industry, because demand for magnesium alloys has been increasing in these branches [2, 3]. Despite several studies were performed on preparation and characterization of such Mg-Zn based materials, majority of authors have dealt with materials prepared by rapid solidification [8]. Also any systematic study on compacting of such materials is missing to our best knowledge. Therefore, in this paper, we investigated preparation of the Mg-Zn alloy containing 50 wt.% of zinc by mechanical alloying and subsequent compacting by SPS. Microstructure evolution between particular preparation steps and hardness of the compacted sample were studied.

2. EXPERIMENTAL SETUP

Elemental powders of Mg (Alfa Aesar, 99.8%, -325 mesh) and Zn (Alfa Aesar, 99.9%, -140+325 mesh) were mixed together in the nominal composition 50 wt.% Mg - 50 wt.% Zn. 5 g of the mixture were batched into a stainless milling vessel of a Retsch PM 100 planetary ball mill with 10 stainless steel balls (20 mm in diameter, 32 g/ball). Before the powders were subjected to a high energy mechanical alloying, the vessel had been filled by an argon atmosphere in order to prevent oxidation. The milling was performed for 1, 2, 3, 4, 5 and 8 hours with a rate of 300 RPM. Influence of milling time was observed on the phase composition studied by X-ray diffraction using a PANalytical X´Pert PRO X-ray diffractometer equipped with a Cu anode (XRD). The powder milled for 8 hours was selected for subsequent compaction implemented by using SPS (heating rate 50 °C/min, sintering temperature 270 °C, sintering time 10 min).

Microstructure of the initial powders, milled powders and the compacted sample was studied. In order to prepare metallographic sections, the powders were molded into an acrylic resin VersoCit, grinded on SiC grinding papers of different grain size and polished on diamond paste (D ~ 0.7 μm) and afterwards on silica suspension (D ~ 0.14 μm). Microstructure of metallographic sections was studied by an OLYMPUS PME3 light metallographic microscope (LM) and by SEM-EDX in BSE regime. Chemical composition of the prepared samples was measured by a TESCAN VEGA-3 LMU scanning electron microscope equipped with an Oxford instruments INCA 350 EDX analyser (SEM-EDX). Using X-ray diffraction phase compositions of the initial and milled powders as well as compacted samples were studied.

Phase transformations were observed on DSC curves measured by a SETARAM-DSC 131 machine. DSC was performed under an argon atmosphere at a heating rate of 5 °C/min in a temperature interval 50 - 300 °C.

In the end two SPS compacted samples were sealed into evacuated quartz ampoules and subjected to a heat treatment (100, 200 °C). Annealing was carried out during 30 minutes in order to study the short-term thermal stability. The changes of microstructure and hardness were then observed. We measured the Vickers hardness HV5.

3. RESULTS AND DISCUSSION

3.1 Mechanical alloying

Morphologies of the powders before and after milling in the planetary ball mill were observed on pictures captured by scanning electron microscope in BSE regime. In **Fig. 1** a comparison of morphologies of the initial

mixture, the powder after 1 hour of milling and the powder milled for 8 hours is shown. In the left picture it is possible to distinguish two different types of particles. Darker ones represent magnesium and lighter ones are particles of zinc. It is obvious that with increasing milling time the particles homogenize (even after 1 hour of mechanical alloying there are no differences in the BSE contrast, which indicates homogenous structure) and become typically sharp-edged.

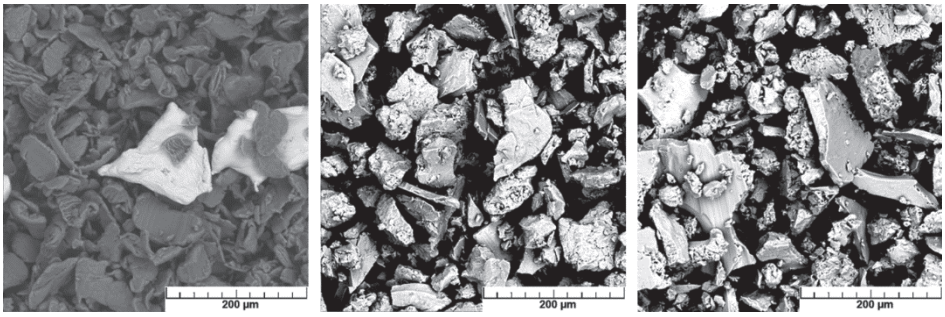

Fig. 1 Microstructures of powders before milling, after 1 hour and 8 hours of milling

In order to determine the influence of milling time, the phase compositions of all powders were studied. They are represented by **Fig. 2**. According to X-ray diffraction patterns the initial mixture contains only Mg and Zn in the elemental form. It is obvious that the mechanical alloying gradually changes the phase composition. Already after one hour of milling a new phase $MgZn_2$ is formed. Presence of elemental zinc decreases and after 2 hours it is completely absent. Powder milled for 4 hours contains also phases Mg_7Zn_3 and Mg_2Zn_{11}. Another 60 minutes lead to creation of Mg_2Zn_3 and disappearance of Mg_2Zn_{11}. Finally, after 8 hours of milling, only metastable phase Mg_7Zn_3 and residual magnesium were proved in the structure. In the case of the mechanically alloyed powders signs of peak broadening can be also observed, which indicates fine structure and high degree of internal stress.

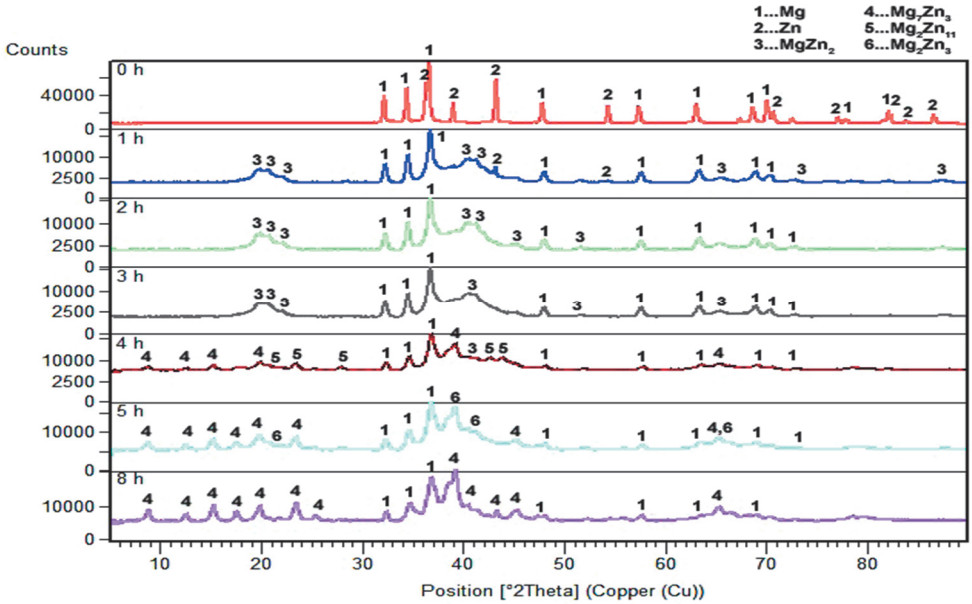

Fig. 2 X-ray diffraction pattern of initial and milled powders

Fig. 3 shows the BSE images and X-ray elemental maps of the initial mixture of powders, a metallographic section of 8 hours milled powder and even the compacted sample. We can see the difference in the distribution of both elements. While in the first column Mg and Zn are strictly located in particles of initial powders, second and third column show homogeneous distribution. Although X-ray diffraction shows presence of two different

phases, we cannot distinguish any contrast differences in X-ray elemental maps, because the available methods are not capable of such a high resolution. Therefore, we can suppose that the inner structure of the milled powders is very fine.

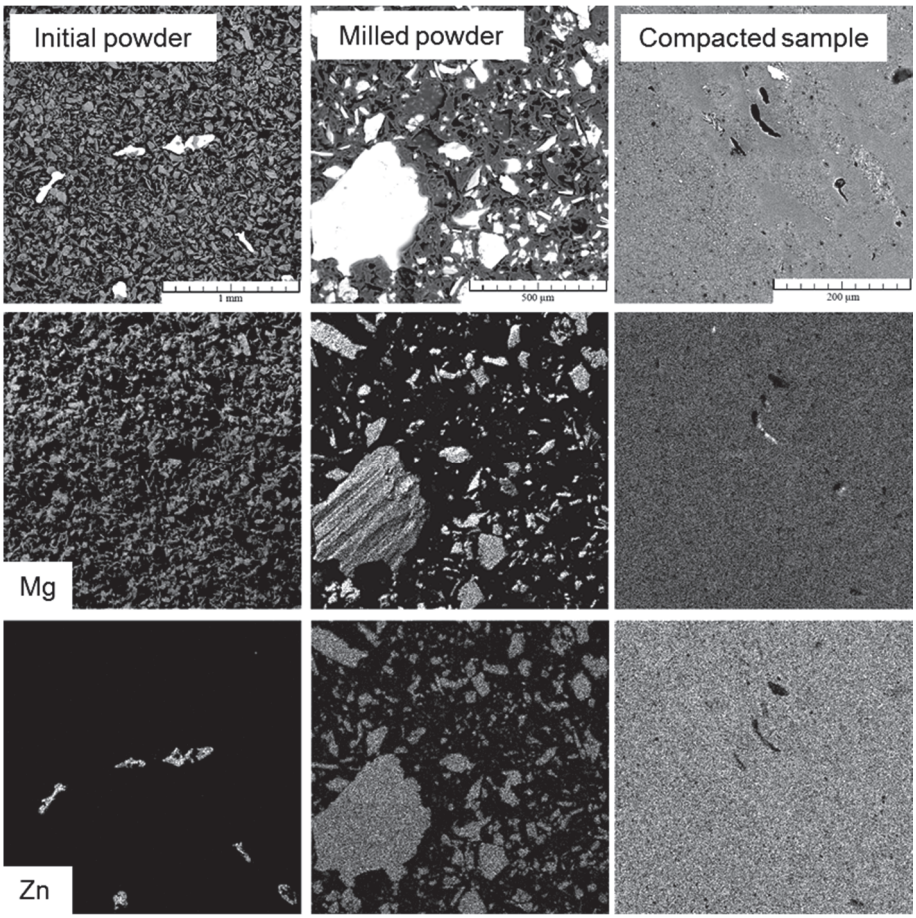

Fig. 3 BSE images and X-ray elemental maps of the initial mixture of powders, a metallographic section of the 8 hours milled powder and the compacted sample

3.1 SPS compacting

The powder milled for 8 hours was selected for subsequent compaction by the SPS method. In **Fig. 3** the third column represents the BSE micrograph and X-ray elemental maps of the compacted sample. Three different areas can be distinguished in the BSE image. However, the EDX analyses did not prove any significant differences in their chemical composition. X-ray elemental maps also show no inhomogeneities in element distribution. As it was mentioned earlier in this paper, the reason is inability of the used method to achieve such a high resolution. In **Fig. 4** the detail picture of the compacted sample can be seen. It displays that the microstructure is very fine with grain size ≤ 2 µm and contains several phases.

XRD analysis was carried out and it identified Mg, MgZn, $MgZn_2$ and Mg_2Zn_{11} phases present in the structure. The XRD pattern of the compacted sample is shown in **Fig. 7**. In comparison with the XRD pattern of the powder before compaction (**Fig. 2**) it can be remarked that the metastable phase Mg_7Zn_3 decomposed into above listed phases.

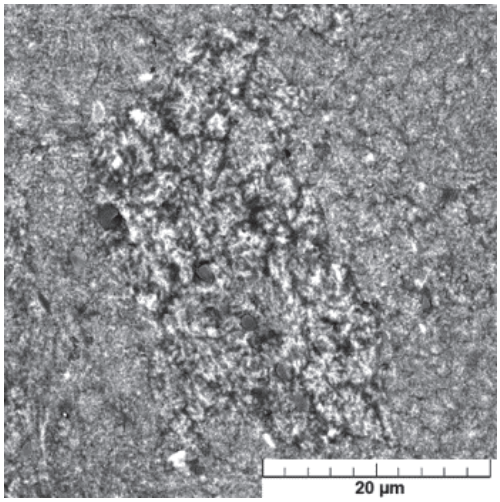

Fig. 4 Microstructure of the compacted sample in detail

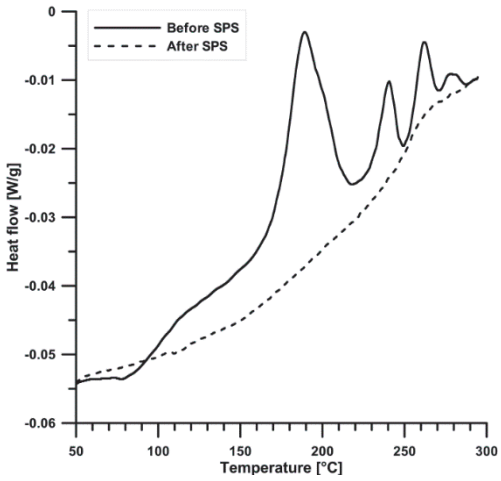

Fig. 5 DSC curves before and after SPS

Changes in phase composition during SPS process as well as thermal stability of the compacted sample were also studied by the DSC analysis. DSC curves are shown in **Fig. 5**. It was found out that four phase transformations occur during heating to 300 °C. Peaks are situated at approximately 190, 240, 260 and 280 °C. Concerning the compacted sample, only a weak exothermic signal was recorded at about 250 °C.

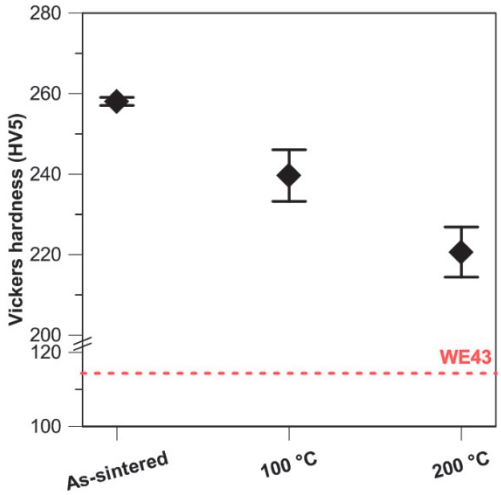

Fig. 6 Hardness HV5 of as-sintered and annealed samples

3.2 Short-term thermal stability

Short-term thermal stability was studied by annealing compacted samples at temperatures of 100 and 200 °C in order to find out if the phase decomposition is completed after the compacting or if there remain any metastable phases. **Fig. 7** represents X-ray diffraction patterns which illustrate that the phase composition does not change. Results of the hardness measurement (plotted in **Fig.6**) show decrease in hardness with annealing temperature, which can be explained by grain coarsening. The sintered sample possessed the highest hardness, 258 HV5, which is really high in comparison with commonly used magnesium-based alloys such as WE43, one of the hardest.

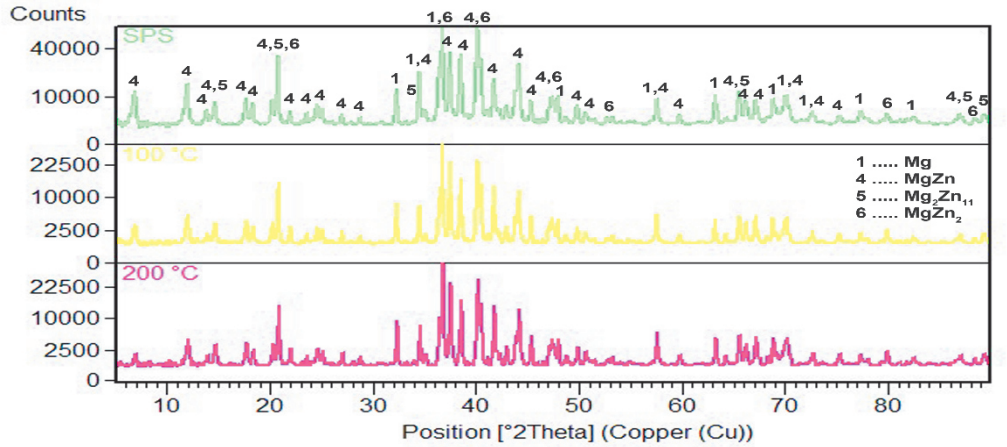

Fig. 7 X-ray diffraction patterns of the SPS compacted sample and thermal treated samples

CONCLUSION

In this paper, the Mg-Zn alloy containing 50 wt.% of Zn was prepared by mechanical alloying. Mechanical alloying was performed for different times and the development of phase composition was observed. The selected sample (after 8 hours of milling) consisted of very fine and homogeneously distributed Mg and Mg_7Zn_3 phases. The powder material was then compacted by the SPS method, during which the metastable Mg_7Zn_3 phase decomposed and new phases were created (Mg, MgZn, $MgZn_2$, Mg_2Zn_{11}). Microstructure of the compacted sample was composed of different areas and possessed hardness about 260 HV5, which is significantly higher than WE43 alloy, one of the hardest commercially used magnesium-based materials. Investigation of short-term thermal stability did not show any changes in phase composition, only hardness decreased thanks to the grain coarsening.

ACKNOWLEDGEMENTS

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