Structural studies on nanocrystalline $Mg_{66-x}Zn_{30}Ca_4NM_x$ alloys (where: NM = Au, Ag and x = 1, 2, 3) obtained by mechanical synthesis

M. Karolus[1a], S. Lesz[2], A. Gabryś[2], K. Gołombek[3], M. Kremzer[4]

[a] *malgorzata.karolus@us.edu.pl*

[1]*Institute of Materials Engineering, University of Silesia, Pułku Piechoty 1A, 41-500 Chorzów, Poland*
[2]*Department of Engineering Materials and Biomaterials, Silesian University of Technology, Konarskiego 18a, 44-100 Gliwice, Poland*
[3]*Materials Research Laboratory, Silesian University of Technology, Konarskiego 18a, 44-100 Gliwice, Poland*
[4]*Nanotechnology and Materials Technology Scientific and Didactic Laboratory, Silesian University of Technology, Towarowa 7a, 44-100 Gliwice, Poland*

Keywords: Mg-based alloy; high energy mechanical alloying, noble metals

The magnesium-based alloys are widely used in the construction of the automotive, aviation and other technical applications. Apart from that, magnesium and its alloys might be used as well as potential materials for medical applications as biomedical implants due to their properties such as specific porosity, fine-grained structure and isotropic properties. In addition, such alloys are characterized by good biocompatibility, biodegradability, lightweight, and appropriate corrosion behavior for this kind of application [1-3]. The mechanical properties and the elastic modulus of magnesium are especially important as the more they are comparable to the natural human bone, the lower the possibility of inducing stress shielding in a bone [4]. The low corrosion resistance of pure magnesium is a flaw in conventional engineering applications, but for biomedical applications it is an advantage. So, it is important to find new manufacturing techniques and process parameters that will allow for a unique microstructure of magnesium-based alloys with controlled corrosion characteristics that are acceptable to the human body.

A promising material for biomedical applications are magnesium-based alloys enriched with noble metals (NM). For the purposes of this study, the $Mg_{66-x}Zn_{30}Ca_4NM_x$ alloys (where: NM = Au, Ag and x = 1, 2, 3) were obtained using the mechanical synthesis process in a high energy ball mill (8000D Mixer/Mill, SPEX SamplePrep, Metuchen, NJ, USA). The paper presents the structural analysis of the alloys milled by 13, 20 and 30 hours, reflecting the transition state of the material, i.e. the state in which the transition phases are just starting to form in the material, and the processes occurring as a result of mechanical synthesis are not finished yet. This choice of research material gives a good overview of

the nanostructure formation mechanisms and its properties in the tested alloys depending on the type and amount of noble metals (Au and Ag; 1, 2, 3 at.%).

The X-ray diffraction analysis (XRD; Empyrean PANalytical Diffractometer, Almelo, Netherland) and scanning electron microscopy studies (SEM; Carl Zeiss, Jena, Germany) with energy-dispersive spectroscopy (EDS; Thermo Scientific, Waltham, MA, USA) were performed to the structural analyses, powder morphology and chemical composition of studied alloys determination. The structure characterization based on the Rietveld refinement, crystallite size determination based on Williamson-Hall theory and the particle size of milling products analysis were carried out (FRITSCH Milling and Sizing ANALYETTE 28 ImageSizer, Fritsch, Weimar, Germany), as well.

Analysis of the diffraction patterns of alloys with the addition of silver indicate a slightly different nature of the processes taking place in the material. In both cases (Au and Ag addition) the presence of the following phases is observed: MgZn2, solid solution based on Mg and Zn residue, however, the amorphization process and nanostructure formation takes place differently. The crystallite size of the main phases present in the studied alloys obtained for different alloys, ie $MgZn_2$ and the magnesium-based solid solution Mg (X) (where X = Zn, Ca, NM), are at the level of 300 - 500 Å, and the parameters of unit cells slightly change.

The tested alloys show similarities in the morphology of the samples. The SEM images show grains of varying degrees of fragmentation depending on the grinding time and areas characterized by the presence of agglomerates. In most cases, it can be seen that the statistical number of particles with characteristic diameters (D10, D50 and D90) is comparable for all tested alloys and the determined mean particle size of the alloys is in a range: D10 = 10 μm, D50 = 30 μm, D90 = 70 -100 μm. The obtained differences may indicate the formation of larger particles at individual stages of grinding as a result of secondary agglomeration and joining of particles with each other during the processes of mechanical synthesis

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

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