The effect of structural changes on the mechanical properties of the Mg-1\%Zn-0.2\%Ca alloy processed by ECAP

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Abstract. The structure of the magnesium alloy Mg-1\%Zn-0.2\%Ca after equal-channel angular pressing (ECAP) has been studied by optical and scanning electron microscopy. It was established that increasing the equivalent strain by increase a number of passes through a ECAP die leads to more pronounced grain refinement in the alloy. When equivalent strain achieved 7.2, an average grain size of 2 μm was observed. It was shown that the ECAP samples enable to demonstrate the high microhardness of 69.5 HV and the enhanced ultimate tensile strength of 282 MPa, which is more than 2 times higher in comparison with the homogenized state, while maintaining ductility.

1. Introduction
The creation of new biodegradable materials is one of the priority directions in the development of materials science for the needs of medicine. As a result a durable implant degrading with a controlled speed, which does not have a harmful effect on the human body [1-3] and performs its functions during the time needed to repair the damaged bone (12-14 weeks) has been developed. Magnesium, which can be used in biodegradable implants, is of special attention by specialists, because it is completely biocompatible[1].

The difficulty is that pure magnesium is unstable and dissolves very quickly in the high chloride environment of the physiological system, thereby losing its functions before the bone is fully restored. Increasing the strength characteristics of magnesium can be achieved due to of a large number of solutes. However, because of the solubility of the alloy in the human body, the choice of alloying elements is significantly narrowed, they must be biologically inert[4,5].

Moreover, it was found that as a result of a high content of alloying elements, secondary phases are formed in the alloys, which are barriers to the movement of dislocations during plastic deformation and, accordingly, the ductility sharply decreases in the alloy. Thus, a weakly alloyed Mg-1\%Zn-0.2\%Ca alloy was selected in which the volume fraction of the secondary phases is minimized.

The selected alloying chemical elements are not toxic to the body and do not cause negative consequences [6-9]. In addition it is known that grain refinement can be used to increase the strength of various metals and alloys, including Mg alloys [10-13]. At the same time for application in medicine it is important to produce bulk ultrafine-grained materials, for example, by equal channel angular pressing (ECAP). However there are only limited publications about microstructure and properties of the Mg-Zn-Ca alloys processed by ECAP [14]. Therefore, the purpose of this work was to identify the evolution of the structure in the process of ECAP and its impact on mechanical properties of the Mg-1\%Zn-0.2\%Ca.
2. Experimental

As the initial material for the studies, the cast Mg-1%Zn-0.2%Ca alloy was chosen. The initial cast samples were subjected to homogenization annealing at a temperature of 450°C for 24 hours with cooling into water. Heat treatment of the samples was carried out in a muffle furnace Nabertherm. The refinement of the structure was carried out by equal-channel angular pressing (ECAP). ECAP was carried out in a die-set with a channels intersection angle of 120° at a speed of 6 mm/min on samples with a diameter of 20 mm after preheating the billet at a pressing temperature of 20 minutes.

To reveal the evolution of the structure, several ECAP regimes were tried. In case of regime #1, two pressing passes were carried out at a temperature of 400°C. Incase of regime #2, two passes were added at a temperature of 350°C to the existing two passes at a temperature of 400°C. Under regime #3 to the available two passes at a temperature of 400°C, two passes at a temperature of 350°C were added two more passes at a temperature of 300°C. In case of regime #4, two passes were added at a temperature of 250°C to two passes at a temperature of 400°C, two passes at a temperature of 350°C, and two passes at a temperature of 300°C. The equivalent strain in case of regimes #1, 2, 3 and 4 was 1.8, 3.6, 5.4 and 7.2, respectively.

The macrostructure was examined with an Olympus GX51 optical microscope. The microstructure analysis was performed with a JEM-6390 scanning electron microscope (SEM) with accelerating voltages of 10 kV. The microhardness (HV) was measured by the Vickers method on a Micromet 5101 measurement tool with a load of 50 g and a dwell time of 10 s. Tensile tests were performed on an Instron 5982 testing machine at room temperature and initial strain rate of 10⁻³ c⁻¹ using specimens with a gage dimension of 0.6×1×4.5 mm³. For each condition, a minimum of 5 samples was tested.

3. Results and Discussion

The structure of the Mg-1%Zn-0.2%Ca alloy after homogenization annealing consisted of equiaxed grains of α-Mg with an average size of 270 μm (Fig. 1a). In the body of the grains there were also Mg₂Ca particles up to 1 μm in size, and at the boundary the size of these particles was 4 μm, the total volume fraction of Mg₂Ca particles in the Mg-1%Zn-0.2%Ca alloy samples was 4%. The annealing twins of various sizes were clearly seen in the structure of all the investigated samples (Fig. 1b).

Figure 1. Structure of magnesium alloy Mg-1%Zn-0.2% Ca in the initial state: a - optical microscopy; b - scanning electron microscopy.

After two ECAP passes one observes the grain refinement (Fig. 2a). However, the structure is highly heterogeneous in volume. Approximately 40% of the structure is occupied by regions with elongated grains. In there maining volume, equiaxed grains with an average size of 5.1μm were formed. Particles in the structure were not detected. A possible and most probable reason may be their refinement and transformation into a finely dispersed form. With an increase in the number of ECAP passes to four, an even finer structure with an average grain size of approximately 4.0 μm is formed (Fig. 2b). However, the heterogeneity is still observed, because separate areas with elongated grains are clearly seen. More homogeneous structure was formed with the number of ECAP passes equal to 6. The average grain size was 3.7 μm (Fig. 2c). The smallest average grain size of 2 μm and a homogeneous structure (Fig. 2d) was produced after a total number of passes equal to 8.

The microhardness of the alloy in the homogenized coarse-grained samples was 42.3 ± 4.8 HV. Structural changes in the ECAP process led to an increase in the microhardness. Thus, after two ECAP passes, the microhardness is increased to 49.6 ± 5.6 HV, and after 4, 6 and 8 passes to 59.5 ± 5.8, 63.1±6.3 and 69.5±6.7HV, respectively (Fig. 3). Obviously, the greater is the degree of strain, the
smaller is the average grain size and the higher is the microhardness. Accordingly, the highest values of microhardness (69.5 ± 6.7 HV) were achieved at the highest equivalent strain (7.2) and the smallest average grain size (2μm).

Figure 4 shows the tensile curves of the alloy under study for different ECAP samples. The Mg-1%Zn-0.2%Ca alloy, in the homogenized state has a higher strength (138 MPa) than pure magnesium (35 MPa [14]). In the deformed state, its properties improved gradually, as expected, with an increase in the equivalent strain. So, after two passes the ultimate tensile strength was only 150 MPa, after four and six passes it reached the values of 205 and 240 MPa, and after eight ECAP passes increased to 282 MPa, which is two times higher than in the initial state.

Also, the yield stress was significantly increased from 34 MPa in the initial state to 205 MPa after deformation by ECAP with a total number of passes equal to 8. Based on the results obtained, it can be concluded that the average grain size significantly influences the strength of the alloy - the smaller is the average grain size, the higher is the strength.

**Figure 2.** Structure of the samples of Mg-1%Zn-0.2% Ca alloys after ECAP: a - 2 passes, b - 4 passes; c - 6 passes; d - 8 passes.
According to the literature data the increase in the strength of magnesium alloys is implemented via refinement of the average grain size. However, in comparison with the known data [15], such high values of the ultimate tensile strength for this alloy were obtained for the first that is attractive for application in medicine to improve the design of implants. It can also be seen from the tensile curve that after two and four ECAP passes, a decrease in the elongation to failure is observed. This effect is probably associated with the formation in the structure of areas with elongated grains that embrittle the material. As the number of passes increases, the ductility increases slightly due to the formation of a homogeneous structure throughout the sample volume.

4. Conclusion

The microstructure and mechanical properties of the Mg-1%Zn-0.2%Ca alloy, promising for use in biodegradable implants after deformation by the equal-channel angular pressing, were investigated. It was shown that an increase in the equivalent strain led to the formation of a more homogeneous structure with a smaller average grain size.

The smallest average grain size (2 μm) was achieved at the highest equivalent strain (7.2). The structural parameters obtained during this deformation provided the greatest increase in the ultimate tensile strength up to 282 MPa, which is two times higher than the homogenized sample (138 MPa). At the same time a ductility did not deteriorate that is of great interest and makes this alloy promising for
its use as a material for manufacturing bioresorbable implants.

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