Influence of the microstructure of Mg-Ca magnesium alloy with TiO$_2$/ZrO$_2$ nano-oxide ALD coating on the functional properties

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Abstract. The paper presents an analysis of the results of evaluating the effect of microstructure obtained by methods of severe plastic deformation (SPD) - equal-channel angular pressing (ECAP) and high-pressure torsion (HPT) - on the mechanical and operational properties of the Mg-1%Ca alloy. The influence of the ZrO$_2$ nano-oxide coating deposited using the atomic layer deposition (ALD) technology was considered in comparison with the uncoated material under study. At the same time, it was noted that the application of a ZrO$_2$ nano-oxide coating by the ALD method made it possible to increase the mechanical characteristics of the ECAP samples by about 20% (the ultimate strength was 205 MPa after ECAP and 262 MPa for ECAP samples with ALD coating). The lowest values of the adhesive component of the friction coefficient were observed on samples after SPD treatment using the HPT method with an applied ZrO$_2$ nano-oxide coating. However, it was found that both the initial material of the study and after SPD treatment by ECAP, the Mg-1% Ca alloy demonstrates a slightly lower damping ability during the deposition of ZrO$_2$ films.

1 Introduction

Biomedical magnesium alloys, used in orthopedics and traumatology as load-bearing implants (plates, screws and pins), are highly biocompatible, hypoallergenic, bioinert, and nontoxic [1, 2], but one of the disadvantages of these materials is their low strength. To increase the strength and functional properties of magnesium alloys, alloying with various elements is used, but this approach is not always acceptable for materials intended for use in medical implants due to the possible adverse effects of some alloying elements on the human body.

The technologies used for deformation processing of metal materials (methods SPD - ECAP and HPT) make it possible to achieve a high-strength state due to the formation of an ultra-fine-grained and nanocrystalline microstructure, which helps to improve the mechanical and functional properties [3]. However, the influence of increasing the dispersion of the microstructure of magnesium alloys on the mechanical, corrosion, tribological (adhesive),

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damping and biological properties remains insufficiently studied. This work aims to fill this gap. The influence of ZrO$_2$ and TiO$_2$ nanooxide coatings deposited by the ALD method, in comparison with the studied materials without coatings, on their functional characteristics is also considered.

2 Research methods and materials

The material for the study was a low-alloy magnesium alloy Mg-1%Ca with a coarse-grained structure after casting and pre-pressing, as well as with an ultra-fine-grained and nanocrystalline structure after SPD treatment by ECAP and HPT. In addition, nano-oxide coatings of ZrO2 and TiO2 were applied to the samples under study using the atomic layer deposition method.

From the analysis of the results of a virtual full factorial experiment modeling the processes of the deformation of the Mg-1%Ca magnesium alloy by equal-channel angular pressing (ECAP) and high-pressure torsion (HPT), regression equations were obtained, which enabled formalizing the examined deformation processes [4]. The modeling procedure and results were published in [5, 6].

The regression equations are given below (equations (1) and (2) correspond to the process of modeling of ECAP, and equation (3) corresponds to the process of modeling of HPT):

\[ Y_1 = 29.15 \cdot X_0 - 0.95 \cdot X_1 + 2.1 \cdot X_2 - 1.5 \cdot X_1 \cdot X_2 \]  \hspace{1cm} (1)
\[ Y_2 = 1.79 \cdot X_0 - 0.063 \cdot X_1 + 1.143 \cdot X_2 - 0.0025 \cdot X_1 \cdot X_2 \]  \hspace{1cm} (2)
\[ Y = 5.56 \cdot X_0 + 1.52 \cdot X_1 - 0.065 \cdot X_2 + 0.91 \cdot X_1 \cdot X_2 \]  \hspace{1cm} (3)

where for equations (1) and (2), ($X_1$) is the processing temperature and ($X_2$) is the number of processing cycles; for equation (3), ($X_1$) is the number of processing cycles and ($X_2$) is the processing temperature. ($Y_1$) and ($Y_2$) are the response parameters (for ECAP) – deformation force and strain intensity, respectively. ($Y$) is the response parameter (for HPT) – strain intensity.

The number of processing cycles that contributed to an increase in deformation force due to strain hardening and a considerable increase in strain intensity [5] was found.

For instance, at a deformation rate of 1.0 mm/s the temperature was about 250–300 °C. The minimum number of cycles should be at least 4. During the SPD processing by HPT, the number of revolutions of the upper unit under a constant hydrostatic pressure (6 GPa) and a lower temperature have the greatest effect on strain intensity.

The implemented numerical model recommends the deformation processing of the Mg-1%Ca alloy by HPT at room temperature with a number of revolutions from 3 to 5. In order to produce a greater effect and to work through the microstructure, it is possible to increase the number of revolutions.

![Fig. 1. Position of the microhardness measurement points.](image-url)
The conducted physical experiments adjusted the developed numerical model and the ECAP processing regimes. The processing route was divided into two stages: 4 cycles at a temperature of 230 °C and 4 cycles at a temperature of 200 °C. This raised the microhardness of the samples under study by approximately 25%, from the initial 53.3 HV to 71.1 HV, while providing a high post-deformation ductility.

Figure 1 shows the position of the Vickers microhardness measurement points.

Mechanical tensile tests were also carried out to determine the tensile strength. For tribological studies to determine the adhesion component of the friction coefficient, a single-ball adhesimeter was used [7]. Metallographic studies were carried out using an Olympus GX51 optical microscope, a JEM-6390 scanning electron microscope, a JEM-2100 transmission electron microscope, and also using X-ray analysis. Potential dynamic polarization curves were used to measure the corrosion potential of materials, and dynamic thermomechanical analysis was used to measure the damping properties of materials.

### 3 Research results

The hardness values of the tested materials are presented in Table 1. The results demonstrate that the hardness of the Mg-1%Ca alloy increases by about 10 HV after ECAP and HPT processing. Besides, the hardness of each position for the ECAP- and HPT-processed alloys is closer, which indicates that their mechanical properties become more uniform. These results are attributed to grain refinement and a more uniform distribution of Mg2Ca.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Position</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>Average (HV)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extrusion</td>
<td></td>
<td>55.7</td>
<td>55.8</td>
<td>57.9</td>
<td>56.9</td>
<td>54.1</td>
<td>56.1</td>
<td>1.43</td>
</tr>
<tr>
<td>ECAP</td>
<td></td>
<td>66.1</td>
<td>66.6</td>
<td>66.3</td>
<td>65.0</td>
<td>65.9</td>
<td>66.0</td>
<td>0.61</td>
</tr>
<tr>
<td>HPT</td>
<td></td>
<td>66.0</td>
<td>66.6</td>
<td>66.4</td>
<td>65.2</td>
<td>65.4</td>
<td>65.9</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Tensile mechanical tests and metallographic studies found that after SPD processing by ECAP, a structural and phase state was formed that provided an approximately two-fold increase in ultimate tensile strength (UTS), from 98 MPa in the homogenized state to 205 MPa in the ECAP-processed state.

Research showed that the application of a ZrO2 nano-oxide coating by atomic layer deposition (ALD) on the surface of the studied material after ECAP processing had the most prospects. Under the assumed conditions of the physical experiment conducted on a nano scratch tester, no separation of the ZrO2 nano-oxide ALD coating with a thickness of 15–20 nm was observed.

Tribological studies revealed that a decrease on grain size enabled reducing the values of the shear strength of adhesive bonds and the adhesion component of the friction coefficient [5, 6]. For instance, the strength of adhesive bonds decreased by about 9% after ECAP processing and by 35% after HPT processing [5]. Meanwhile, the adhesion component of the friction coefficient decreased by about 18% after both types of processing [5]. Hydroxyapatite (HA), used in the tribological tests as a bone tissue simulator, promotes a decrease in both the shear strength of adhesive bonds and the adhesion component of the friction coefficient, irrespective of the structural state of the material under study. The presence of HA on the contact surfaces in the initial state reduced both parameters by approximately 24%, after ECAP processing – by about 37% and after HPT processing – by about 18% [5]. Research found that the lowest values of the strength of adhesive bonds and the adhesion component of the friction coefficient were observed for the samples after SPD processing by HPT with the ZrO2 nano-oxide ALD coating present on the contact surfaces,
both with and without a bone tissue simulator in the form of HA suspension. The adjusted medium integral values of the friction coefficients decrease as a result of the processing. This is caused by strain hardening resulting from grain size reduction.

Research found that when the ZrO₂ nano-oxide coating was applied on the material surface after the two types of processing, the friction coefficient values were stabilized and practically did not depend on the preceding SPD processing. The application of the ZrO₂ nano-oxide coating by ALD further increased the mechanical characteristics of the ECAP-processed samples by over 20% (UTS was 205 MPa after ECAP processing and 262 MPa for the ECAP-processed samples with an ALD coating).

Fig. 2 shows the curves of potential dynamic polarization (PDP) of the extruded substrate from the alloy and the substrate from the ECAP-processed alloy. To simulate a biological environment, the samples were immersed in the standard solution at a temperature of 37 °C during the PDP test. In Figure 2, the voltage at the intersection of the cathodic and anodic curves is defined as the corrosion potential \(E_{\text{corr}}\) of the material. The larger is the corrosion potential value, the higher is corrosion resistance. Besides, the corrosion current density \(I_{\text{corr}}\) is calculated using the Tafel interpolation method. The data for \(E_{\text{corr}}\) and \(I_{\text{corr}}\) are summarized in Table 2. It can be seen from Table 2 that the corrosion current density of the ECAP-processed alloy is somewhat lower than that of the extruded alloy. ECAP processing can make the distribution of the Mg₂Ca phase more uniform, thereby reducing galvanic corrosion that emerges between the \(\alpha\)-Mg matrix and the Mg₂Ca phase. However, the grains of the ECAP-processed alloys are fine and have multiple grain boundaries that may easily become the starting point for corrosion. Due to these factors, improvement in the corrosion resistance of the alloy after ECAP processing is not obvious.

![Potential dynamic polarization curves for the substrate from the extruded alloy and for the substrate from the ECAP-processed alloy.](image)

Fig. 2. Potential dynamic polarization curves for the substrate from the extruded alloy and for the substrate from the ECAP-processed alloy.

In order to find out which film had the best protective capability in a physiological environment, two types of ALD films, ZrO₂ and TiO₂, were applied on the extruded alloy, and their corrosion resistance was analyzed. The results are shown in Figure 3(a) and Table 2. As demonstrated in Table 2, the extruded alloy with the ZrO₂ film has a lower corrosion current density than the alloy with the TiO₂ film, which means that the ZrO₂ film provides a better corrosion protection.

Since the ZrO₂ nano-oxide film ensures an excellent corrosion resistance, the further analysis of PDP was performed using the ZrO₂ coating applied on the extruded alloy and the ECAP-processed alloy, respectively. The results are shown in Figure 3(b) and Table 2. As
shown in Table 2, the corrosion current density of the ZrO$_2$ film applied on the ECAP-processed alloy is lower than that of the extruded alloy with the ZrO$_2$ film. This result indicates that the corrosion protection of the ZrO$_2$ film applied on the ECAP-processed alloy is more efficient than that of the film applied on the extruded alloy.

![Fig. 3. Potential dynamic polarization curves. (a) Extruded alloy without any films, or with the TiO$_2$ or ZrO$_2$ films, (b) the ZrO$_2$ film applied on the extruded alloy or the ECAP-processed alloy.](image)

**Table 2.** Hardness test results.

<table>
<thead>
<tr>
<th></th>
<th>Bare Extrusion</th>
<th>Bare ECAP</th>
<th>TiO$_2$ Extrusion</th>
<th>ZrO$_2$ Extrusion</th>
<th>ZrO$_2$ ECAP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{corr}$ (V)</td>
<td>-1.97</td>
<td>-1.96</td>
<td>-1.58</td>
<td>-1.61</td>
<td>-1.72</td>
</tr>
<tr>
<td>$I_{corr}$ (A/cm$^2$)</td>
<td>9.39·10$^{-5}$</td>
<td>7.66·10$^{-5}$</td>
<td>5.51·10$^{-6}$</td>
<td>4.67·10$^{-7}$</td>
<td>1.34·10$^{-7}$</td>
</tr>
</tbody>
</table>

In order to examine the difference between the ZrO$_2$ nano-oxide ALD films on the extruded and annealed alloy and on the ECAP-processed alloy, the crystalline structures were studied using X-ray diffraction analysis, and the results are shown in Figure 4.

![Fig. 4. XRD results for the ZrO$_2$ film on the extruded alloy and on the ECAP-processed alloy.](image)

As it is demonstrated in Figure 4, a higher peak intensity of the ZrO$_2$ film on the ECAP-processed alloy is observed, which indicates a better screening capacity of the ZrO$_2$ film applied on the investigated alloy after ECAP processing.

DTA (dynamic thermomechanical analysis) was used to measure the damping properties of the extruded alloy and the ECAP-processed alloy without with and without the ZrO$_2$ films. The damping efficiency is presented by the tangent $\delta$. The higher is the tangent $\delta$, the better is the damping capacity. The experimental results are shown in Figure 5.
Without the ZrO$_2$ film, the damping capacity of the extruded alloy was better than that of the ECAP-processed alloy. This phenomenon may be explained with the help of the Granato-Lücke dislocation damping model. Since the Mg-Ca phase of the ECAP-processed alloy is finer and more uniformly distributed, dislocation motion is hindered, which does not contribute to the dissipation of vibrational energy. Both the extruded and ECAP-processed alloys exhibit a somewhat lower damping capacity when the ZrO$_2$ films are deposited. This phenomenon may be related to the fact that during the ALD of the film the temperature is maintained at a level of 200 °C for about 4 hours, which reduces the dislocation density, thereby decreasing vibrational energy dissipation and reducing the damping capacity.

4 Conclusion

From the study it follows that intense plastic deformation by ECAP and HPT methods effectively increases the strength of the material under study – a magnesium alloy of composition Mg-1%Ca. It was found that applying a ZrO$_2$ nano-oxide coating using the ALD method made it possible to increase the mechanical characteristics of ECAP samples by approximately 20% (the tensile strength was 205 MPa after ECAP and 262 MPa for ECAP samples with an ALD coating). In addition, the tribological properties in the contact pair “magnesium alloy of composition Mg-1%Ca – bone tissue” are improved. The lowest values of the adhesive component of the friction coefficient were observed on samples after SPD treatment using the HPT method with an applied ZrO$_2$ nano-oxide coating. At the same time, the SPD treatment has virtually no effect on the corrosion and damping properties.

A nano-oxide film of the ZrO$_2$ composition deposited using atomic layer deposition technology has better protective properties against corrosion (a lower corrosion current density was observed) compared to a TiO$_2$ film. It has been established that (both the initial material of the study and after ECAP treatment) the Mg-1%Ca alloy demonstrates a slightly lower damping capacity during the deposition of ZrO$_2$ films.

This, SPD processing for the subsequent manufacture of implants from the hardened magnesium alloy Mg-1%Ca due to a significant strength increase may be a solution for the task of minimization of the implant design elements.

References


