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COMMUNICATION

DOI: 10.1002/adem.201500176

Enhancement of the Mechanical Properties of an Mg–Zn–Ca Alloy Using High-Pressure Torsion**

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The structure and properties of an Mg–Zn–Ca alloy processed by high-pressure torsion (HPT) are investigated. Microstructure is studied by transmission electron microscopy, scanning electron microscopy, and X-ray diffraction. An enhanced microhardness of 990 MPa is observed in the HPT-processed samples due to an uniform microstructure with a grain size of 150 nm. After additional annealing at 200 °C, the ultrafine-grained alloy demonstrates an ultimate tensile strength of 270 MPa with a ductility of 9%.

Mg and its alloys show great potential in biomedical applications due to its biocompatibility, low density, high strength-to-weight ratio, elastic modulus comparable to bone, and biodegradability.[1–4] It is known that magnesium alloys containing Al, Zn, Mn are toxic for human body.[5] Therefore, an alloy of the Mg–Zn–Ca system has been chosen for investigations,[6–10] because of low-toxicological effects on human body. The dissolution rate and tensile strength of Mg-based alloys having different contents of Zn and Ca have been considered in ref.[7,11,12] In particular, it has been observed that the content of Zn should not exceed 1%,[7,11] and the content of Ca is recommended to be within 0.3%.[12] On the basis of these observations, the Mg–1%Zn–0.13%Ca has been selected for investigations. It is known that the magnesium alloys of this system demonstrate rather weak mechanical properties. At the same time recent studies have shown that the application of severe plastic deformation results in the grain refinement of conventional magnesium-based alloys leading to significant enhancement of strength.[13–18] The aim of this work is to study the influence of grain refinement on the enhancement of mechanical properties of a Mg–Zn–Ca alloy processed by high-pressure torsion (HPT).

1. Materials and Experimental Procedures

Cast magnesium (Mg–1%Zn–0.13%Ca) alloy homogenized at 430 °C for 1 h and quenched in water was used as the starting material. To create an ultrafine-grained structure in samples HPT method was used. At this method the sample (diameter 20 mm and thickness 0.9 mm) was placed between two anvils, applying a uniaxial pressure of 6.0 GPa and then rotating the lower anvil (5 rotations). HPT method is ideal for processing hard materials at room temperature because of large hydrostatic pressure.[19]

Microstructure observation was performed using a scanning electron microscope (JEM6390) and a transmission electron microscope (JEM2100) with an accelerating voltage of 30 and 200 kV, respectively. The grain size was measured by linear intercept method and calculated using more than 250 grain measurements. Foils were prepared by twin jet polishing with the help of the solution of nitric acid–30% and methanol–70% electrolyte to conduct electron microscopic analysis.

To determine the lattice parameters a and c, the root-mean-square strains, and the size of coherent scattering domains D, the X-ray diffraction analysis was carried out on CuK_α radiation (=1.78892 A) using a Rigaku diffractometer. X-ray diffraction (XRD) patterns were taken from an area from half of radius to edge of the HPT disk.

The mechanical properties of the samples were investigated using microhardness (H_V) measurements and tensile tests.

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[**] *O. Kulyasova would like to acknowledge the support from the Russian Foundation for Basic Research. This work was supported under project No. NK 14-02-31662\14. R. Islamgaliev would like to acknowledge the support from the Russian Ministry of Education and Science within the basic part of the program for universities. R. Z. Valiev also thanks the Russian Federal Ministry for Education and Science for the support (RZV Grant No. 14.B25.31.0017).*

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All of the microhardness measurements were taken using a Micromet-5101 device by the Vickers method. One sample from each set of homogenized and HPT samples was chosen for investigation microhardness. Each sample was cut on 8 sectors and tested across the radius of each disk in incremental steps of 0.5 mm. The microhardness was measured with an applied load of 100 g and a test time of 10 s. The variation of the results of the microhardness measurements was 1%. To study thermal stability the samples were subjected to annealing for 30 min in the temperature range of 100–350 °C.

Tensile tests have been performed at room temperature at a strain rate of $10^{-3}\,s^{-1}$ on a specially designed computer-controlled testing machine operating with a constant displacement of the specimen grips.[20] The gauge of the tensile test samples was 2 mm in length, 1 mm in width, and 0.6 mm in thickness.

2. Results and Discussion

Figure 1a shows typical microstructures observed in the magnesium alloy subjected to homogenization at 430 °C. One can see that this treatment leads to coarse-grained structure with an average grain size of about 30 μm. Bright elongated particles (Figure 1a) with a length of about 20 μm were observed at grain boundaries, and particles of 1 μm in length and 0.5 μm in thick were observed in grain bodies. Their volume fraction was of about 9%. Formation and phase composition of such particles have been studied earlier.[11,21] Their composition corresponds to the $Ca_2Mg_6Zn_3$ phase. In the initial microstructure, studied by TEM, these particles were observed as well (Figure 1b).

TEM studies demonstrated that an ultrafine-grained structure with an average grain size of about 150 nm can be observed in the alloy after HPT processing (Figure 1c, d). The mechanism of grain refinement during HPT has already been discussed.[22] Inhomogeneous diffraction contrast observed in grain interiors was caused by a high density of defects and distortions of a crystalline lattice. In particular X-ray diffraction demonstrated the enhanced root-mean-square strains of 0.234 in the HPT samples in comparison with 0.0057 in the initial state. The $Ca_2Mg_6Zn_3$ particles were retained in the structure (Figure 1d), their average size did not change essentially.

Also, dispersed particles with a size of 10 nm were observed in the structure of the HPT-processed samples (Figure 1e). From precise investigations by electron diffraction patterns we found that the interplanar distances of these particles belong to the Mg_2Ca phase (Figure 1e, f). It can be noted that this phase was observed also in samples from alloys of this system after extrusion, as reported elsewhere.[7]

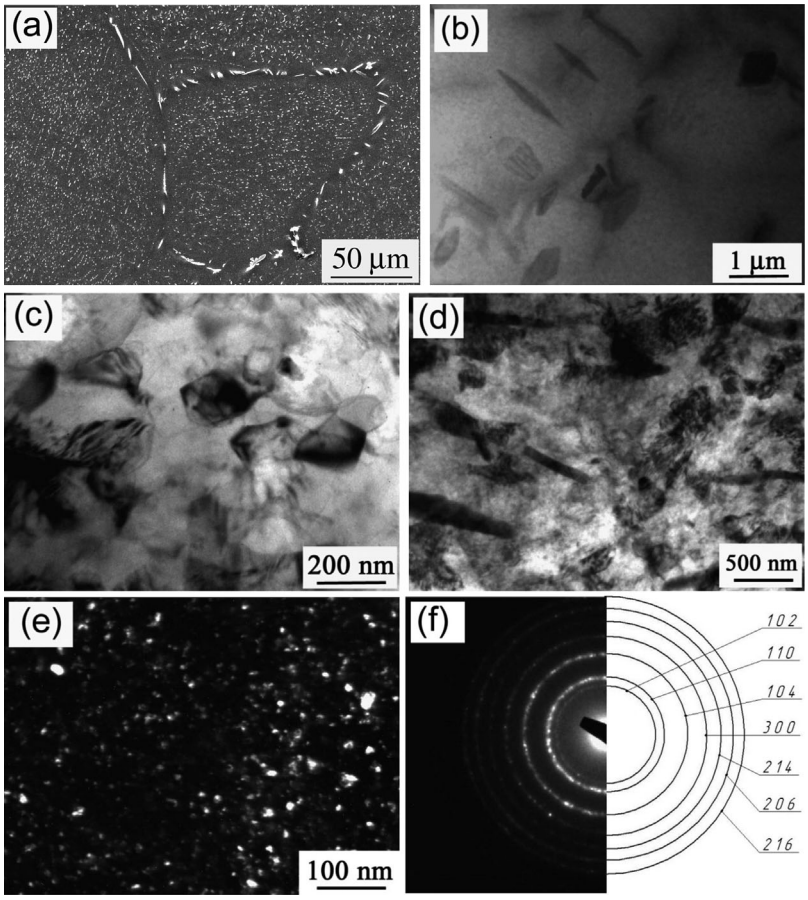

Fig. 1. Structure of the Mg–Zn–Ca alloy: (a, b) initial state: (a) (SEM), (b) TEM; (c–f) after HPT (TEM): (c) bright-field image; (d) bright-field image of $Ca_2Mg_6Zn_3$ particles; (e) dark-field image of Mg_2Ca particles; (f) electron diffraction pattern from Mg_2Ca particles.

The dislocation density was reduced and the average grains size increased up to 450 nm in the HPT samples after additional annealing at 150 °C (Figure 2a). The $Ca_2Mg_6Zn_3$ particles were also observed in the structure (Figure 2b) with a length up to 1 μm and width up to 0.5 μm. The volume fraction of the precipitations was about 7%. Note should be made that in the structure of the samples after annealing at 150 °C, the Mg_2Ca particles were observed, thier average size was increased up to 50 nm (Figure 2a).

The microstructure of the HPT samples after additional heating at 200 °C had a rather uniform microstructure (Figure 2c–f). From the Figure 2c we can clearly see that the average grain size was increased up to 1.5 μm. The $Ca_2Mg_6Zn_3$ particles remained stable (Figure 2d, e) with the similar size to samples after HPT and additional annealing at 150 °C. The Mg_2Ca particles were also observed, with the average size of 50 nm (Figure 2f). The dislocation density was reduced significantly (Figure 2e, f).

The average size D (nm) of coherent scattering domains (CSD) of HPT-processed samples determined by X-ray diffraction was 73.4 nm. After additional annealing at 200 °C, the CSD value was 117.4 nm, and the root-mean-square

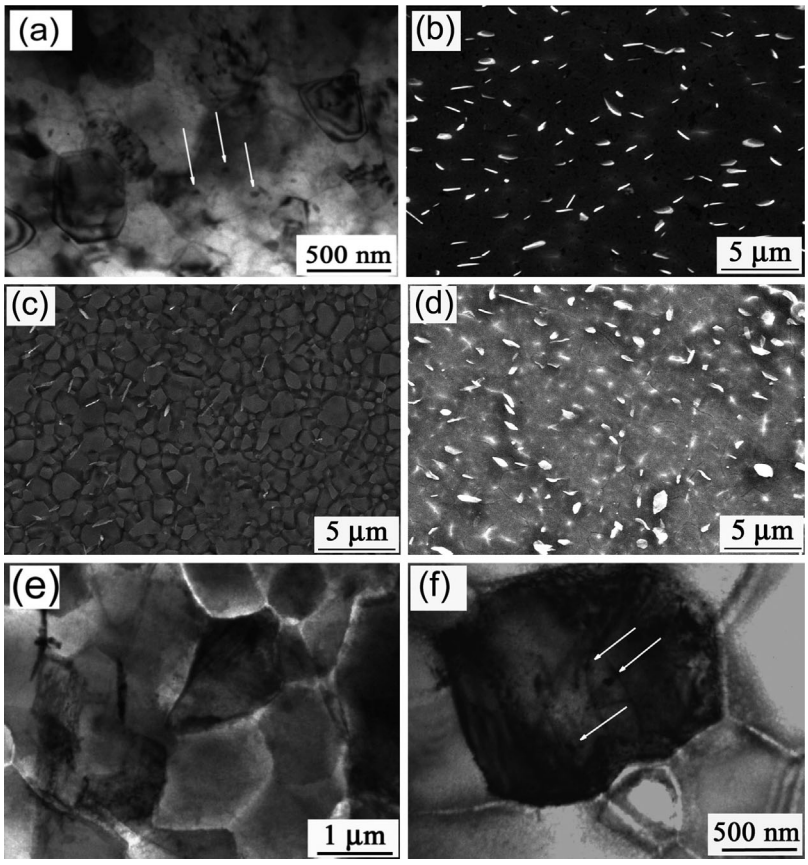

Fig. 2. Microstructure of the Mg–Zn–Ca alloy after HPT and annealing at different temperatures: (a, b) at 150 °C; (c–f) at 200 °C. (a) bright-field image (TEM); (b) size of $Ca_2Mg_6Zn_3$ particles (SEM); (c) average grain size (SEM); (d) size of $Ca_2Mg_6Zn_3$ particles (SEM); (e) TEM image of grain structure; (f) TEM image of Mg_2Ca particles.

strains of the samples with a UFG structure decreased to 0.026%. Obviously, the redistribution and annihilation of dislocations leads to relaxation of internal stresses and beginning of grain growth at this temperature.

Microhardness of the initial coarse-grained Mg–Zn–Ca alloy was of about 450 MPa. Significant grain refinement (Figure 1b, c) which is took place at the HPT process led to increase of microhardness in the samples up to 990 MPa (Figure 3a). Microhardness of the HPT samples after additional heating diminishes and after annealing at 350 °C is reduced to 450 MPa (Figure 3a).

As can be seen from Figure 3a, at the annealing temperatures of 150 and 200 °C high values of microhardness are retained, and relaxation of internal stresses is expected, therefore this temperatures were selected for a detailed study of the microstructure and mechanical properties.

The coarse-grained Mg–Zn–Ca alloy had an ultimate tensile strength of 140 MPa and an elongation of about 13% (Figure 3b).[23] The extended stage of strain hardening in the samples of magnesium alloy can be connected with the formation of deformation twins during tensile testing.[13] After HPT processing and additional annealing at 150 °C, the samples failed in a brittle manner without achieving the yield stress, because the samples after HPT processing had high internal elastic stresses. At the same time the enhanced ultimate tensile strength of 270 MPa and a ductility of 8.5% was demonstrated in the HPT samples after heating at 200 °C. The enhanced strength is conditioned obviously by grain refinement and dispersion hardening whereas a high strain hardening (the increase of the flow stress with strain) can be explained by the activation of dislocation slip in non-basal planes, as observed earlier on the example of other UFG Mg alloys.[24]

3. Conclusions

The application of HPT leads to formation of ultrafine-grained structure in the magnesium Mg–Zn–Ca alloy with an

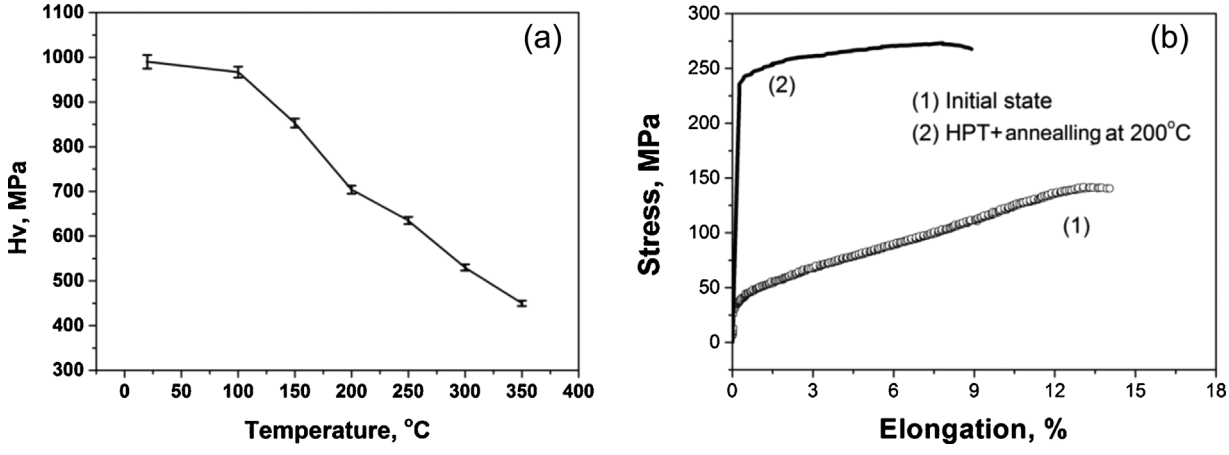

Fig. 3. (a) Variation of microhardness of the Mg–Zn–Ca alloy after HPT depending on the annealing temperature; (b) tensile tests of Mg–Zn–Ca at room temperature and strain rate of 10^{-3} s^{-1}: (1) initial coarse-crystalline state, (2) after HPT and additional annealing.

average grain size of 150 nm. After annealing of the SPD-produced samples at a temperature of 200 °C, the average grain size was increased up to 1.5 μm. HPT processing and additional annealing at 200 °C results in a higher ultimate tensile strength (270 MPa) as compared to the initial coarse-grained samples (140 MPa). The enhancement of UTS can be explained by grain refinement and dispersion hardening; whereas, the retention of a good ductility (8.5%) is obviously conditioned by the activation of dislocation slip in non-basal planes. The observed significant enhancement of the alloy's properties after grain refinement is very attractive for medical applications, since it allows improving the design of implants, and may also have a favorable effect on its functional properties.

Article first published online: September 19, 2015
Manuscript Revised: August 12, 2015
Manuscript Received: March 31, 2015

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