STRUCTURE AND PROPERTIES OF MG-MN ALLOY AFTER EQUAL CHANNEL ANGULAR PRESSING WITH BACKPRESSURE AT ROOM TEMPERATURE

Erik ŠVEC, Jan DUCHOŇ, Viera GÄRTNEROVÁ, Aleš JÄGER

Institute of Physics of the AS CR, v.v.i., Na Slovance 2, 182 21 Prague 8, Czech Republic

Abstract
In this work Mg-Mn binary alloy was processed by Equal Channel Angular Pressing (ECAP) with backpressure (BP) at room temperature (RT) and material properties were subsequently investigated. Route Bc was employed for multiple passes by ECAP-BP and specimens were processed 3 and 4 times via ECAP die with channel angle 90°. It is shown that multiple passes (up to 4) result in crack-free structure. The microstructure observed by electron back scatter diffraction (EBSD) and transmission electron microscopy (TEM) revealed significant grain refinement with an average grain size estimated to be ~0.5 - 0.6μm. This is one of the lowest grain sizes available in literature for Mg alloy after ECAP. Thermal stability was examined by dilatometry up to 480°C. The results show first structural instability at ~80°C during heating in both samples. For thorough characterization tensile tests at RT and at strain rate of 10⁻³s⁻¹ were also conducted after 3 and 4 passes by ECAP-BP. Ultimate tensile strength (UTS) was found to be surprisingly low ~122 MPa for Mg-0.2wt.%Mn after 4 passes.

Keywords: Magnesium, ECAP, backpressure, EBSD, TEM

1. INTRODUCTION
Magnesium alloys are often considered as prospective materials for hydrogen storage [1]. These so called magnesium hydrides are safe and capable to store even more hydrogen than pressure and cryogenic storage tanks. Crucial issues connected with suitable material for hydrogen storage via hydrides are sufficiently fast diffusion paths for absorption and desorption, thermal stability of the structure for absorption and desorption cycling at elevated temperature and the amount of bounded hydrogen [2]. Bulk nanostructured materials, notably magnesium, often show remarkable advantages with respect to hydrogen storage capability due to excess of defects that serve as traps for hydrogen. Bulk nanostructured materials can be prepared by severe plastic deformation (SPD).

Equal channel angular pressing (ECAP) is one of the most attractive method of the SPD techniques because it can produce bulk billets for subsequent metallurgical operations. Many parameters such as number of passes, processing route, speed, temperature or backpressure have been already considered [3].

Recent activities led to find suitable materials for absorption and desorption of hydrogen into the structure – to produce so called hydrids. Mg-H hydrids are promising hydrogen - absorbing materials with large gravimetric capacity (~7.6 wt.%) [1] [2].

Magnesium alloys are also very attractive for use as structural materials in the automotive industry and aeronautic because of good strength-to-weight ratio [4] and as biodegradable materials. The aim of this paper is correlation between structure and properties of Mg-Mn binary alloy subjected to ECAP-BP at room temperature.

2. EXPERIMENTAL
Mg-Mn alloy was prepared from 99,9% Mg and 99,9% Mn in an induction furnace under the protection of argon atmosphere, then homogenized at 500°C for 10h and cooled in furnace. Chemical composition of the alloy was measured by X-ray fluorescence (XRF) and verified by flame atomic absorption
spectromentry (F AAS). For ECAP ingot was machined into 10x10x55 mm billets. ECAP was proceeded with channel angle 90° at room temperature following route Bc, pressing speed was 0.4 mm/s and the backpressure 150 - 400 MPa. Tensile tests were performed with INSTRON 5882 at strain rate $10^{-3}$ s$^{-1}$ and at room temperature with dog-bone tensile specimen dimensions 12 mm long, 4 mm wide and 1.5 mm thick. Samples for transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) analysis were prepared from ECAPed billet in longitudinal plane by ion milling (Gatan PECS) and then observed with FEI Tecnai G2 F20 X-TWIN. EBSD data were obtained by Dual Beam FEI Quanta 3D FEG. Thermal dilatometric analysis (NETZSCH 402) up to 480°C in argon atmosphere and with heating/cooling rate of 2°C/s was employed to discover thermal stability of the fine grained Mg-Mn alloys. Coefficient of thermal expansion (CTE) was calculated as derivated curve $\Delta L/L_0=f(T)$

3. RESULTS AND DISCUSSION

Tab. 1 show chemical composition of the alloys used in this work. Two techniques were used to validate chemical composition: X-Ray Fluorescence (XRF) and Flame Atomic Absorption Spectrometry (F AAS). The experiment demonstrated a maximum of three ECAP passes for Mg-1.5wt.%Mn and four passes for Mg-0.2wt.%Mn.

Tab. 1 Chemical composition of the Mg-Mn binary alloys used in this work

<table>
<thead>
<tr>
<th>Label</th>
<th>Number of ECAP passes</th>
<th>XRF</th>
<th>F AAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>3</td>
<td>1.45 % wt. ± 0.04</td>
<td>1.56 % wt. ± 0.02</td>
</tr>
<tr>
<td>Sample 2</td>
<td>4</td>
<td>0.23 % wt. ± 0.02</td>
<td>0.21 % wt. ± 0.01</td>
</tr>
</tbody>
</table>

3.1. TEM observations

Fig. 1 shows TEM microstructure of sample 1 and sample 2. From both TEM figures is evident strong grain refinement after ECAP-BP.

The high energy stored in the material in the form of defects causes low distinctness and contrast and it is difficult to define exact grain boundaries and structural features. A sample 2 (Fig. 1 right) shows better definition of grain and grain boundaries than sample 1 (Fig. 1 left). This can be a consequence of lower Mn content. Grain size was estimated ~0.5μm and ~0.6μm for sample 1 and sample 2, respectively.
3.2. TEM - EELS analysis

Many insoluble particles were found in the microstructure by TEM observations, mainly in the sample 1, because of it’s higher amount of Mn in comparison with a sample 2. Thus, TEM-EELS method was used to analyse chemical composition of insoluble particles in sample 1. This technique acquires a spectra of insoluble particle that correspond with occurrence of particular elements. A maximum solubility of manganese in magnesium at the peritectic temperature is 2.46%wt. And decreases rapidly with temperature approaching zero at room temperature [5]. Fig. 2 shows TEM micrograph with analyzed particle denoted by red arrow. The size of these particles was in the range from 1 to 1000 nm. Fig. 3 shows two EELS spectra for Mg and Mn, which proves that insoluble particle is virtually Mn. This result corresponds with Smith who concluded that in the binary Mg-Mn system there are no intermetallic phases formed and that the precipitates are α manganese [6].

![TEM - EELS](image)

Fig. 2 Left: TEM - EELS of Mg (up) and Mn (down) of the sample after 3 passes by ECAP-BP at RT. Right: Analyzed insoluble particle, red arrow.

3.3. SEM - EBSD observations

SEM – EBSD analysis was performed in order to confirm TEM observations, notable grain sizes. Fig. 3 (left) shows grain boundaries of the sample 2 with coloured marking of specific range of boundary angles. The initial structure is significantly refined during four passes of ECAP-BP. The average grain size of the specimen is <1 μm, that reasonably-well correlates with TEM observation. This value is one of the smallest grain sizes of Mg alloys subjected to ECAP [7]. Fig. 3 (right) shows histogram of grain boundaries distribution. First peak belongs to low angle grain boundaries (LAGBs). High amount of LABs is a result of SPD at low homologous temperature. As shown by Ostapovets et al., maximum at 30° can correspond with coincident site lattice (CSL) grain boundaries [8] [9]. According to CSL model this maximum match with Σ15b and Σ17a, eventually Σ15a and Σ13a. The last peak around 90° are {10-12} twin boundaries.
Fig. 3 Results of EBSD analysis of sample 2. Left: grain boundaries superimposed with image quality map. Right: histogram of misorientation angles. The inset in the histogram show color coding for the left figure.

3.4. Thermal stability

Thermal dilatometric analysis (TDA) was performed to find out critical temperatures for microstructural stability. The thermal expansion curves for Mg-Mn alloys were measured with two thermal (heating and cooling) cycles (runs).

Fig. 4 Temperature dependence of a) the relative elongation for sample 1 (1.run), b) the CTE for sample 1 (1.run), c) the relative elongation for sample 1 (2.run), d) the CTE for sample 1 (2.run)

The temperature dependence of the relative elongation for three passes ECAP-BP specimen in the first thermal cycle is plotted in Fig. 4a and temperature dependence of the CTE in Fig. 4b. Fig. 4b shows a noticeable decrease of CTE over the temperature range from 80 up to 180°C during heating, in comparison with the temperature variation of CTE in the second thermal cycle (Fig. 4d). Influence of the strain in the specimen produced during ECAP-BP is also significant in the temperature range from 180°C up to 480°C.
during the first run (Fig. 4b) in comparison with second run (Fig. 4d). During first run heating, the values of CTE of both samples are lower than those for cooling. The temperature dependence of the relative elongation for sample 2 in the first thermal cycle is plotted in Fig. 5a and temperature dependence of the CTE in Fig. 5b. After first run the specimen was annealed and the course of the second run (Fig. 5d) is approximately linear in the range from RT to 480°C for both heating and cooling process. This means that there were no irreversible changes and all accumulated strain was released during first thermal cycle. During first run heating of sample 2 was observed much lower decrease of CTE in temperature range from 80 up to 160°C (Fig. 5b) than in sample 1. Next course of the curve shows increasing of CTE similar to second run curve (Fig. 5d). These measurement shows that the thermal stability is influenced by both composition and number of passes.

![Fig. 5 Temperature dependence of a) the relative elongation for sample 2 (1.run), b) the CTE for sample 2 (1.run), c) the relative elongation for sample 2 (2.run), d) the CTE for sample 2 (2.run)](image)

3.5. Mechanical properties at room temperature

Plots of engineering stress versus engineering strain are shown in Fig. 6 for Mg-Mn alloy tested at room temperature at an initial strain rate of $10^{-3}$ s$^{-1}$.

![Fig. 6 Engineering strain versus engineering stress curves measured at room temperature and at strain rate $10^{-3}$s$^{-1}$ for sample 1 and sample 2](image)
Reduction in grain size usually improves strength according to Hall-Petch relation [10]. It has been found that strength level is not significantly improved in ultra-fine grained Mg-Mn, contrary to coarse grained Mg. This is probably caused by strong texture that can be developed during ECAP of Mg at RT [11].

CONCLUSIONS

Mg-Mn alloy was processed via ECAP-BP at RT with following results. Maximum number of ECAP-BP passes for Mg-0.2wt.%Mn alloy (sample 2) is four and for Mg-1.5wt.%Mn (sample 1) three. Both samples demonstrate similar thermal stability. Sample 1 shows higher ultimate tensile strength, but lower elongation than three ECAP passes specimen with 0.2wt.%Mn. Grain size was estimated ~0.5μm and ~0.6μm for sample 1 and sample 2, respectively.

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