Structure and mechanical characterization of Mg-Nd-Zn alloys prepared by different processes

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Abstract. Magnesium alloys containing about 3 wt. % of Nd and 0.5 wt. % of Zn are considered as promising materials for application in transport and medical industry. Properly treated materials can reach ultimate tensile strength (UTS) higher than 300 MPa. Also the corrosion resistance of these alloys is superior to many other magnesium-based materials. Present work is focused on the preparation of Mg-3Nd-0.5Zn magnesium alloy by classical casting and subsequent thermal treatment. As-cast material was extruded at 400 °C, with extrusion ratio equal to 16 and velocity of 0.2 mm/s. The effect of thermal treatment and also strong plastic deformation during extrusion on final structure conditions and mechanical properties is specified. Present results confirm significant improvement of tensile yield strength (TYS) and UTS after extrusion process as a consequence of fine-grained structure combined with precipitation strengthening. Beside, texture strengthening in the direction parallel to the extrusion has been observed too.

1 Introduction

Thanks to low density and improved mechanical and corrosion properties specific magnesium-based alloys are of a great interest in aviation and automotive industry [1]. The main drawback is application of magnesium alloys at high temperatures due to their low yield strength [2]. However, the superior magnesium alloys containing rare earth elements and yttrium preserve their mechanical properties up to 300 °C [3]. Another utilization magnesium alloys find in medicine as materials for biodegradable implants. There is tendency to reduce or substitute alloying elements in order to reduce price and increase biocompatibility of this material [4]. In many works yttrium is replaced with cheaper zinc [1], [2], [5]. Zinc is biocompatible element essential for human body [6]. It can improve mechanical properties by solid solution hardening and age hardening. However amounts higher than 1 wt.% leads to another precipitation sequence, which is associated with hardness decrease [1], [2]. Neodymium is relatively abundant rare earth element with maximum solubility in Mg 3.6 wt.% at eutectic temperature [4]. It seems to be good alloying element because it significantly improves mechanical properties by solid solution strengthening and by precipitation hardening [7]. It also increases corrosion resistance by forming Nd₂O₃ oxide layer on the surface [8]. Pure magnesium is highly susceptible to galvanic corrosion especially with contained impurities like Fe, Ni, Cu, Co. Fe is...
insoluble in Mg-matrix and there is tolerance limit about 170 ppm of Fe in pure Mg. However, the influence of impurities works differently in Mg-RE alloys because rare earth elements trap impurities in intermetallic compounds, reducing the threat of galvanic corrosion [9].

Reduction in amount of alloying elements is beneficial for increasing biocompatibility of magnesium alloys, which are considered as materials for biodegradable implants. Those materials will degrade in a body after fulfilling their function without the necessity of subsequent removal. This will reduce the cost of healing process and increase comfort of the patient. Magnesium and its alloys have ideal mechanical properties for this purpose. The elastic modulus of magnesium is about 42 GPa, which is very close to the natural bone (3-20 GPa). Such values prevent the bone stress shielding and help with better bone ingrowth [5].

Mg-Nd-Zn system is well known for its good mechanical properties and good corrosion resistance. Those properties depend highly on the preparation method and structure [10]. Mechanical properties of Mg-Nd-Zn alloys can be improved by suitable heat treatment. It is associated with the formation of Guinier-Preston (GP) zones during precipitation. The precipitation process occurs as follows: solid solution, GP zones, \( \beta'' \text{Mg}_{3}\text{Nd} \) cph phase, \( \beta' \text{Mg}_{3}\text{Nd} \) (fcc), \( \beta \text{Mg}_{12}\text{Nd} \) phase [7].

Another way how to improve mechanical properties is an extreme plastic deformation associated with recrystallization and grain refinement. One of the processes how to attain fine structure is extrusion [11]. During extrusion process the material is extremely plastically deformed. Based on the material and procedure conditions, the final product is composed of fine recrystallized grains, but also some elongated grains which were not recrystallized [12]. However, magnesium alloys are prone to the texture formation in the extruded material. After extrusion process, basal planes of hexagonal structure are preferably oriented parallel to the extrusion direction for many magnesium-based alloys [13]. This has great impact on the anisotropy of mechanical properties. Rare earth elements can partially suppress formation of such a specific texture [14].

2 Materials and methods

2.1 Preparation of samples
Mg-3Nd-0.5Zn (composition in wt. %) alloy was prepared from pure Mg (99.9 wt.%), Nd (99.8 wt.%) and Zn (99.9 wt.%) in induction furnace under inert argon (99.996 wt.% atmosphere. The melt was homogenized at 750 °C for 15 minutes followed by casting into cylindrical brass mold with 50 mm in diameter and 150 mm in height (labeled as as-cast). Three cylindrical samples were prepared by this way. One of them was then heat treated at 540 °C for 16 hours followed by quenching in water (labeled as T4). The third as-cast cylinder was extruded at 400 °C with extrusion ratio of 16 and 0.2 mm/s extrusion speed. Final products were rods with 7.5 mm in diameter (labeled as extruded). Impurities were determined by AAS method and the results are summarized in table 1.

| Label      | Co    | Cu    | Ni    | Fe    |
|------------|-------|-------|-------|-------|
| As-cast    | 0.72  | 16.80 | 6.50  | 64.40 |
| T4         | 0.24  | 6.00  | 6.50  | 128.20|
| Extruded   | 0.47  | 14.70 | 4.50  | 72.90 |

2.2 Microstructure
Samples were grinded on SiC grinding papers (P80-P4000) and subsequently polished on diamond paste. The final polishing was done on Topol 2 with fine particles of Al₂O₃. Subsequently samples were etched in solution containing 10 ml of acetic acid, 4.2 g of picric acid, 10 ml of distilled water and 70 ml of ethanol. The microstructure was studied by light microscopy and by electron scanning microscope SEM (TescanVEGA3 with energy dispersion spectrometry and EBSD detector). Phase analyses were performed using X-ray diffraction (XRD, X’Pert Philips, 30 mA, 40 kV, CuKα X-ray radiation)

2.3 Mechanical properties
Compressive tests were performed on LabTest 5.250SP1-VM at room temperature on cylindrical samples with 6 mm in diameter and 9 mm high. Constant deformation speed of 0.001 s⁻¹ was used. Compressive yield strength (CYS), ultimate compressive strength (UCS) and total deformation were
determined. Tensile properties were measured on the same machine at room temperature on samples with 3.5 mm in diameter in constricted area and 25 mm in length. Constant deformation speed of 0.001 s\(^{-1}\) was used. Vickers hardness according to the EN ISO 6507-1 was measured at loading corresponding to 1 kg.

2.4 Corrosion behaviour
Immersion tests were carried out in simulated body fluid (SBF) at 37 °C for 14 days. Table 2 shows SBF composition similar to human plasma. Corrosion rate was determined from weight loss and also from dissolved magnesium by atomic absorption spectroscopy.

| Ions   | Na\(^+\) | K\(^+\) | Mg\(^{2+}\) | Ca\(^{2+}\) | Cl\(^-\) | HCO\(_3\)\(^-\) | HPO\(_4\)\(^{2-}\) | SO\(_4\)\(^{2-}\) |
|--------|----------|---------|-------------|-------------|---------|----------------|----------------|----------------|
| SBF    | 142.0    | 5.0     | 1.5         | 2.5         | 147.8   | 4.2            | 1.0            | 0.5            |

3 Results

3.1 Microstructure
Figure 1 shows microstructures of prepared samples. As-cast ingot has typical dendritic structure, with distance between dendritic branches of 8.3 ± 0.7μm. Alloying elements segregated around dendrites, so there was higher concentration of them. Dendrites consist of α-Mg-matrix and eutectic phase Mg\(_{12}\)Nd (20.4 ± 3.2 wt.% Nd), which was indicated by XRD diffraction. Mg\(_{2}\)Nd phase was also found in a minor amount. Neodymium and zinc are homogenously dissolved in Mg-matrix (1.3 ± 0.4 wt.% Nd, 0.4 ± 0.1 wt.% Zn). The rest of the neodymium is placed primarily in the intermetallic phases and zinc forms intermetallic phases with neodymium too (31.5 ± 3.9 wt.% Nd, 6.7 ± 0.5 wt.% Zn). Those phases still seem to be binary phases, where Nd in the structure is partially replaced by Zn.

The heat treatment was performed according to the very well-known approach used for similar alloys. After the heat treatment the original phases dissolved in the Mg-matrix (2.5 ± 0.9 wt.% Nd, 0.5 ± 0.2 wt.% Zn). However, some eutectic phases precipitated at grain boundaries and inside the grains as well. It denotes that during the thermal treatment material had to be partially melted at some areas. The grain size of resulted material ranged from 100 μm to 500 μm. In figure 1 structure of extruded material is displayed. Intermetallic phases such as Mg\(_{12}\)Nd, Mg\(_{3}\)Nd and Mg\(_{41}\)Nd\(_{5}\) were identified in this state. The amount of neodymium in the Mg-matrix was slightly lower than in the as cast material (1.1 ± 0.3 wt.% Nd, 0.4 ± 0.1 wt.% Zn), which might be caused by precipitation of fine intermetallic phases Mg\(_{41}\)Nd\(_{5}\) in the area of original dendritic segregation. Extrusion led to the partial recrystallization of the material. The size of recrystallized equiaxed grains was about 2.3 ± 1.4 μm, which was confirmed by EBSD analysis. A large part of the structure consisted of elongated strongly deformed grains with the nuclei of new grains separated by small angle boundaries with misorientation between 2 and 15 ° (white lines in Figure 2). Performed analysis also confirmed strong texture in the material after extrusion. It is a common phenomenon for magnesium alloys that cause the anisotropy of mechanical properties.
3.2 Mechanical properties

From mechanical properties, hardness, compressive and tensile tests were carried out (results are summarized in Table 3). After the heat treatment hardness remains almost the same as for the as-cast material. Compressive stress-strain curves (Figure 3) show strong increase in yield strength of the extruded material compared to the as-cast ingot. This enhancement is caused especially by finer grains but also by existence of fine precipitates which were formed during the extrusion. The same reasons affect the observed value of hardness (Table 3). Thermal treatment of the as-cast ingot leads to increase of ultimate compressive strength and ductility. The reason is connected with the lower amount of brittle intermetallic phases in the structure and probably higher grain size, which support twinning, and therefore, contribute to plasticity by this mechanism.

The tensile yield strength of extruded sample is much higher than the compressive yield strength (Table 3). This results from a strong texture that was confirmed by EBSD analysis. Materials-crystallizing in hexagonal structure deforms not only by dislocation slip mechanism but also by specific twinning mechanism. Twinning requires much less energy for plastic deformation, however, it strongly depends on grain orientation [15]. After extrusion the basal planes are oriented parallel to the extrusion direction, which is also the direction of applied compressive force. Such orientation of hexagons towards the compressive force is strongly favourable for twinning mechanism, so it noticeably decreases compressive yield strength of this material. On the other hand, this orientation towards tensile force direction is unfavourable for deformation by twinning, therefore, tensile yield strength is increased [16].
### 3.3 Corrosion behaviour

Corrosion behaviour was studied in SBF solution for 14 days. Weight loss and concentration of magnesium ions in solution were applied as two methods for the estimation of corrosion rate (Table 4). Among studied materials as-cast ingot had the highest corrosion rate.

Thermal treatment led to a rapid decrease of corrosion rate. This is partially caused by more neodymium in the solid solution which has good impact on corrosion rate, although even higher corrosion resistance could be expected if lower amount of intermetallic phases is presented in the structure due to the absence of galvanic cell between magnesium matrix and MgNd phases in the structure. On the other hand, standard reduction potential of MgNd phases is relatively close to Mg, so the Anode-to-Cathode potential difference is low [10]. Therefore, the effect of galvanic corrosion in Mg-Nd alloys is low and the corrosion is more uniform [17]. The extrusion of as-cast ingot also lowered the corrosion rate. This improvement is caused predominantly by finer structure of this material, where grain boundaries accelerate passivation kinetics. Small grains reduce intensity of galvanic corrosion due to formation of close situated anodic-cathodic regions, which should lead to lower corrosion rate and more uniform corrosion [18].

### Table 3: Mechanical properties; CYS = compressive yield strength, UCS = ultimate compressive strength, D = relative deformation, TYS = tensile yield strength, UTS = ultimate tensile strength, E = elongation.

| Sample    | CYS [MPa] | UCS [MPa] | D [%] | TYS [MPa] | UTS [MPa] | E [%] | HV1      |
|-----------|-----------|-----------|-------|-----------|-----------|-------|----------|
| As-cast   | 58±5      | 182±5     | 15.2±0.8 | -         | -         | -     | 53.1±3.1 |
| T4        | 51±5      | 252±30    | 22.0±2.5 | -         | -         | -     | 54.2±3.9 |
| Extruded  | 174±5     | 423±12    | 12.7±0.4 | 251±6     | 271±8     | 2.7±0.7 | 61.1±2.3 |

### Table 4: Corrosion rate [mg/cm²/day].

| Sample    | Weight loss | Ions |
|-----------|-------------|------|
| As-cast   | 1.04±0.18   | 0.83±0.16 |
| T4        | 0.43±0.05   | 0.31±0.07 |
| Extruded  | 0.67±0.07   | 0.59±0.04 |
4 Conclusion
Magnesium alloy designated as Mg-3Nd-0.5Zn was prepared by melting of pure metals. Thermal treatment (T4) was applied on one as-cast ingot to investigate changes in microstructure and mechanical properties. Another as-cast ingot was also extruded. The huge changes were observed between these states in both mechanical and corrosion properties. Significantly improved mechanical properties of the extruded material were connected with finer structure, precipitation strengthening, but also strong texture causing anisotropy of properties in tension and compression. Corrosion rates after the heat treatment or extrusion were about half the value of the as-cast sample. Such improvement was related to the increased Nd concentration in solid solution or fine grained structure, respectively.

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