

# THE INFLUENCE OF ELEMENT Zn ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF AS-CAST Mg-Zn-Y-Nd Magnesium ALLOYS

Ing. Vít Janík

<sup>a</sup> ČVUT Praha, FS, ÚMI, Karlovo nám. 13, 121 35 Praha 2, ČR, [v.janik@centrum.cz](mailto:v.janik@centrum.cz)

## Abstrakt

Slitiny hořčíku jsou v poslední době používány stále častěji i v náročných aplikacích v automobilovém a leteckém průmyslu, kde jsou na ně kladeny zvýšené požadavky z hlediska teplotní a korozní odolnosti. V tomto příspěvku je sledován vliv množství Zn na mikrostrukturu lité hořčikové slitiny typu Mg-Zn-Y-Nd, a to především na fázové složení a podíl ikosahedrické kvazikrystalické fáze I v její struktuře. Dále jsou pro dvě slitiny s rozdílným množstvím Zn sestrojeny vytvrzovací křivky a je diskutován mechanismus precipitace.

The application of magnesium alloys in automotive industry and aeronautics is increasing; increasing are also demands on high temperature and corrosion resistance of these types of alloys. The effect of element Zn on the microstructure of as-cast Mg-Zn-Y-Nd alloy is evaluated in this paper, first of all the effect of Zn on the phase composition and fraction of icosahedral quasicrystalline I-phase in the microstructure of the alloy is concerned. Hardening curves for two alloys with different Zn content are constructed in the next part of this paper, mechanism of precipitation is also discussed.

## 2. INTRODUCTION

Magnesium alloys are intensively used in automotive and aerospace industry in wide range of applications, but there are significant limitations and difficulties too. These alloys provide only low creep and corrosion resistance, therefore research is focused on increasing their mechanical properties with addition of new types of elements. Basic magnesium alloy is commercially used type of AZ91 (Al 9 wt%, Zn 1 wt %) in C, D, E or HP version [1]. In progressive magnesium alloys element Al is replaced with rare earth elements (RE) such as Ga, Dy, Nd and Y. These alloys offer higher corrosion resistance and are also applicable in higher temperature regimes (more than 200°C) [2].

This work is focused on the study of microstructure and mechanical properties of progressive WEZ magnesium alloys with chemical composition Mg-Y-Nd-Zn (Table 1). Increasing amount of Zn in WEZ alloys leads to modification of intercellular eutectic phases, namely their chemical composition and type of crystallographic lattice. Detailed review of all kinds of secondary phases formed in WEZ alloys is beyond range of this paper and can be found in [3]. Table 2 illustrates only some selected phases, which are found in Mg-rich corner of Mg-Zn-Y ternary phase diagram.

**Table 1.** Chemical composition of experimental casts

| Alloy | Zn    | Y    | Nd   | Zr   | Al   | Gd   |
|-------|-------|------|------|------|------|------|
| A     | 12,00 | 3,22 | 1,16 | 0,27 | 0,00 | 0,17 |
| B     | 25,85 | 3,22 | 1,16 | 0,27 | 0,01 | 0,17 |

**Table 2.** Characteristics of binary and ternary phases of Mg-Zn-Y

| Phase                                             | Zn at (-) | Pears. sym.<br>space group | Lattice     | Parameters |        |              |
|---------------------------------------------------|-----------|----------------------------|-------------|------------|--------|--------------|
|                                                   |           |                            |             | a (nm)     | c (nm) | $\gamma$ (°) |
| MgZn                                              | 0,5       | hP12, ?                    | hexagonal   | 2,557      | 1,814  | 120          |
| MgZn <sub>2</sub>                                 | 0,67      | hP12,P6 <sub>3</sub> /mmm  | hexagonal   | 0,5253     | 0,8568 | 120          |
| (Mg)                                              | 0,024     | hP12, P6 <sub>3</sub> /mmc | hexagonal   | 0,3209     | 0,5211 | 120          |
| X - Mg <sub>12</sub> ZnY                          | 0,08      | modulace 18 R              | hexagonal   | 0,322      | 4,699  | 120          |
| W -Mg <sub>3</sub> Zn <sub>3</sub> Y <sub>2</sub> | 0,38      | cF16, Fm <sub>3</sub> m    | cubic       | 0,683      |        |              |
| I - Mg <sub>3</sub> Zn <sub>6</sub> Y             | 0,6       | Fm <sub>53</sub>           | icosahedral | ar = 0,519 |        |              |

The most important secondary phase in WEZ alloys is icosahedral quasicrystalline I phase, which is not very typical in metal materials cooled conventionally from melting temperature (4). Binary stable MgZn and metastable Laves type MgZn<sub>2</sub> are also considered to be important for achieving high mechanical properties of these alloys after thermal treatment, namely solution treatment with consequent ageing at temperature 150-200°C. In contrary, presence of cubic W phase in WEZ alloys is considered to be negative. This phase has less coherent interface with hexagonal lattice of solid solution than icosahedral I phase (5), therefore main goal of development of WEZ alloys is to reduce amount of W phase and increase amount of I phase.

## 2. EXPERIMENTAL PROCEDURE

Base alloy WE54 (prepared in Magnesium Elektron, Manchester) was modified in laboratories of TU Clausthal with different amount of element Zn as can be seen in Table 1. Both alloys were squeeze cast under a protective gas atmosphere (Ar + 1%SF<sub>6</sub>). Experimental specimens were taken from central parts of billets and than were isochronally annealed at 150°C in protective coating from austenitic stainless steel for different times (up to 100 hours). Specimens were cut into two parts; first part was used for metallographic investigation of microstructure and determination of hardness and micro hardness, second part was then thinned and electro polished to thin foils.

Experimental equipment consisted of conventional optical microscope Zeiss Neophot 32, scanning electron microscope JEOL JSM-5410 with secondary electron detector and back scattered electron in COMPO regime and transmission electron microscope JEOL 2000EX equipped with Oxford Instruments EDAX analyzer and selective area electron diffraction (SAED).

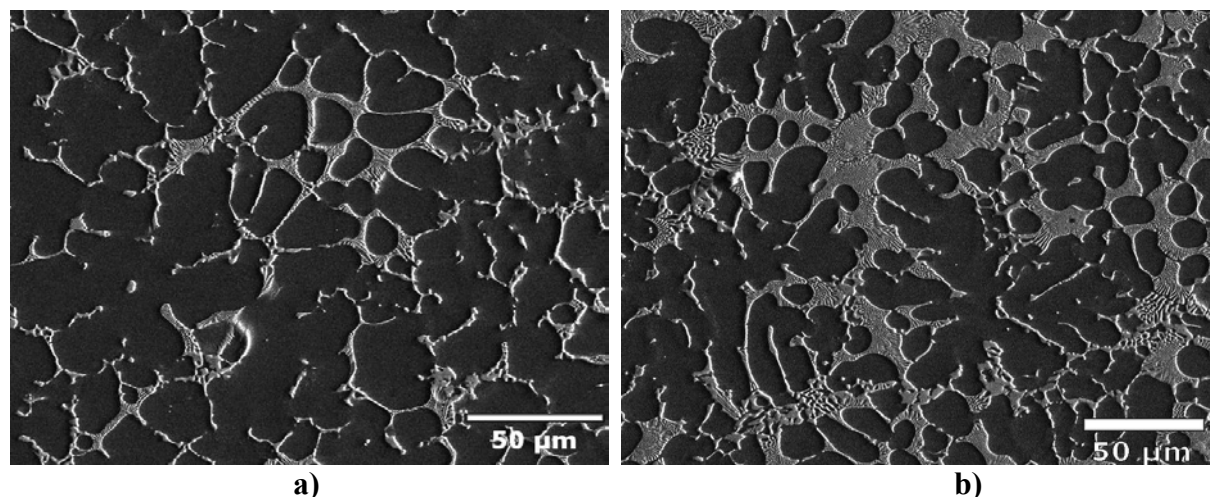
Image analysis was used for determination of area fraction of secondary intercellular phases or eutectics and for average size of dendrite cells. Time dependence of these microstructure characteristics with increasing time of ageing was investigated. Ageing response of both alloys was characterized by measuring of hardness and micro hardness by LECO M-400-G1 and LECO V-100-C devices in 10 sites of central parts of microstructure.

## 3. Results and discussion

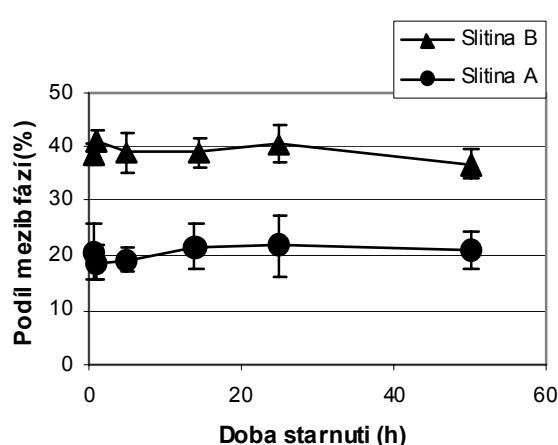
### Microstructure of as-cast and annealed alloys

The as cast alloys exhibit typical dendritic structure with the mean cell size of about 20  $\mu$ m (Fig. 1.), cell size for both alloys is independent on the time of ageing at 150°C (see Fig. 1). Area fraction of eutectics or other intercellular phases is also independent on the time of ageing; however the difference between fraction of eutectics of alloys A and B is unambiguously visible and is caused by higher amount of element Zn in alloy B than in

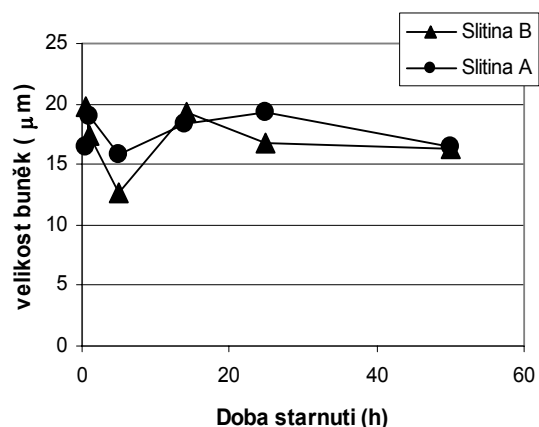
alloy A. Microstructure of both alloys is composed of cells of solid solution of  $\alpha$ -Mg matrix and of different types of eutectics and intercellular phases. Stable and metastable precipitates are situated in  $\alpha$ -Mg matrix, these particles are homogeneously distributed in  $\alpha$ -Mg grains, however quantity and composition of precipitates for both alloys may differ with increasing time of ageing as will be discussed later.



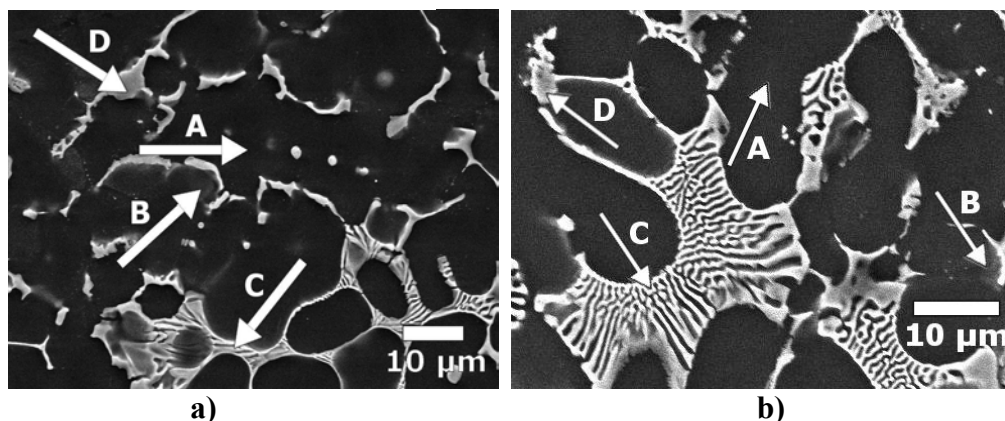
**Fig. 1.** Microstructure of as-cast material a) A – 12% Zn, b) B - 25% Zn; scanning electron microscopy, BSE imaging, etched by 3% nital



**Obr. 2.** Time dependence of intercellular phases



**Obr. 3.** Time dependence of cell size



**Fig. 4.** Phase composition of as-cast material a) A – 12% Zn, b) B - 25% Zn; scanning electron microscopy, BSE imaging, etched by 3% nital

## Phase composition

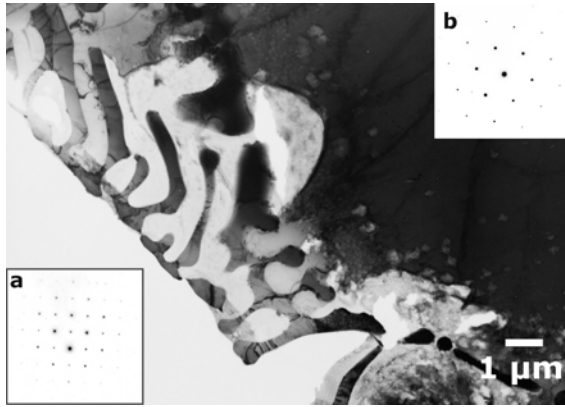
Microstructure taken by scanning electron microscope of alloys A and B is illustrated also on **Fig. 4**. On this picture, different structure phases are marked with arrows and labeled A, B, C or D. Label A seen on **Fig. 4** is solid solution of  $\alpha$ -Mg with hexagonal crystal structure (see **Table 1**), chemical composition and crystal lattice is independent on amount of element Zn in both alloys (also see **Table 3**). Label B corresponds to oversaturated location of solid solution near eutectics with increased portion of precipitates in  $\alpha$ -Mg matrix. Also this location has in both alloys same chemical composition. Lamellae of eutectics are labeled C and massive intercellular phases at grain boundaries which do not contribute to formation of eutectics are labeled D.

Comparison of phases marked C and D in the **Table 3** reveals differences in chemical composition of phases between both alloys. Lamellae of eutectics (localities C) in alloy A contain higher amount of element Y and lower amount of element Zn than lamellae of eutectics in alloy B. Both types of eutectics are illustrated in Figs. 5 and 6. These pictures have been taken by transmission electron microscope of thin foils. Selective Area Electron Diffraction (SAED) from sites C of both alloys is on Fig. 5 (alloy A) and Fig. 6 (alloy B). SAED in [100] direction is on picture a) in lower left corner of Fig. 5. This diffraction pattern illustrates four-fold symmetry of lamella of eutectics. SAED in [111] direction on picture b) – upper right corner of Fig. 5 was taken after rotation of electron beam and illustrates four-fold symmetry of the same lamella of eutectics. Three and four-fold symmetries of diffraction patterns exhibit existence of cubic structure, so that this phase is cubic W phase (see Table 2). SAED in [100] direction on picture in upper right corner of Fig. 6 illustrates five-fold symmetry of lamella of eutectics; this type of symmetry is characteristic for icosahedral quasicrystals, so that phase is I phase from Table 3.

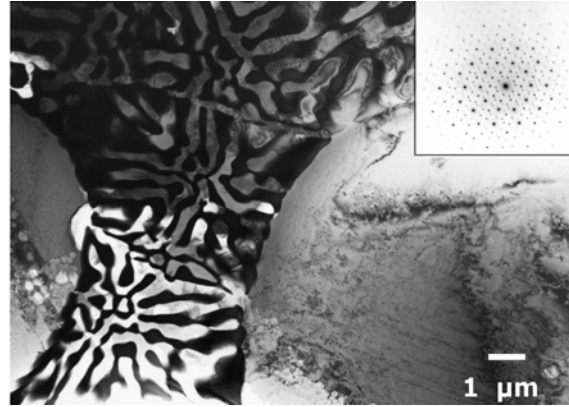
Differences of element Nd amount in localities marked D in alloys A and B leads to conclusion, that phase D could not been interpreted as a single uniform phase, but its type has to be re-considered. Phase D was divided into phase D1, which composition is near phase C (also SAED confirmed similar crystal structures for both alloys) and phase D2, independent on amount of element Zn in both alloys. The crystal structure of phase D2 could not be determined exactly, because SEAD of this phase in both alloys was unable to obtain. On the basis of literature data [4,5] this phase is probably hexagonal  $\beta$  Mg<sub>12</sub>YNd or tetragonal Mg<sub>41</sub>Nd<sub>5</sub> phase with small amount of dissolved Zn and/or Y.

**Table 3.** Approximate chemical composition of A, B, C, D1 and D2 localities measured by EDS chemical analysator

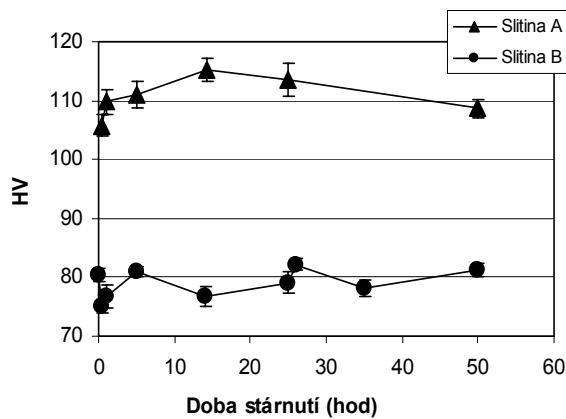
| Alloy A |              |              |              |              |              |
|---------|--------------|--------------|--------------|--------------|--------------|
| element | A            | B            | C            | D1           | D2           |
| Mg      | 97,67 ± 0,20 | 96,49 ± 0,81 | 70,28 ± 2,41 | 48,52 ± 6,53 | 63,91 ± 3,15 |
| Zn      | 2,30 ± 0,18  | 3,46 ± 0,73  | 25,73 ± 2,05 | 45,52 ± 6,48 | 31,93 ± 2,72 |
| Y       | 0,01 ± 0,03  | 0,06 ± 0,10  | 3,53 ± 0,50  | 4,58 ± 2,89  | 0,32 ± 0,32  |
| Nd      | 0,02 ± 0,03  | 0,02 ± 0,02  | 0,47 ± 0,08  | 0,85 ± 0,45  | 3,45 ± 0,15  |
| Alloy B |              |              |              |              |              |
| element | A            | B            | C            | D1           | D2           |
| Mg      | 98,29 ± 0,62 | 92,58 ± 5,38 | 71,81 ± 4,08 | 64,77 ± 3,46 | 58,16 ± 5,36 |
| Zn      | 1,61 ± 0,65  | 6,84 ± 5,81  | 19,01 ± 2,98 | 29,15 ± 2,60 | 37,95 ± 6,65 |
| Y       | 0,06 ± 0,07  | 0,44 ± 0,49  | 7,98 ± 0,95  | 5,20 ± 1,67  | 0,44 ± 0,14  |
| Nd      | 0,04 ± 0,08  | 0,14 ± 0,07  | 1,19 ± 0,37  | 0,87 ± 0,27  | 3,45 ± 1,24  |



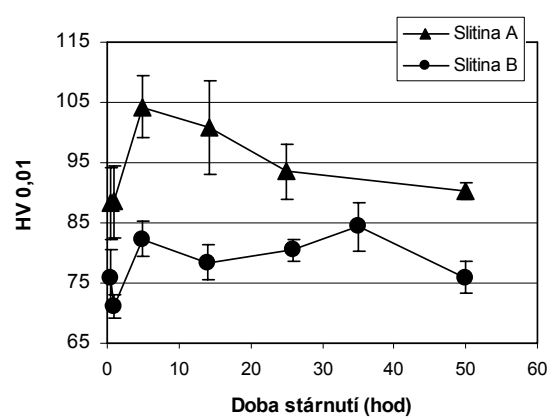
**Fig. 5.** Detail of eutectics of alloy A, aged 5 hours, TEM, a) SAED in [100] axis, four-fold symmetry b) SAED in [111] axis, three-fold symmetry



**Fig. 5.** Detail of eutectics of alloy B, aged 5 hours, TEM, a) SAED in [100] axis, five-fold symmetry



a)



b)

**Fig. 7.** Age-hardening curves for alloys A and B aged at temperature 150°C a) hardness, b) micro hardness of cells of solid solution

### Age-hardening response



**Fig. 8.** Alloy B, aged for 5 hours, needle-shaped particles in [0001]  $\alpha$ -Mg direction in solid solution, TEM bright field image

Time dependence of hardness and micro hardness of both magnesium alloys is illustrated on Fig. 7. Alloy B in as-cast state reach higher value of harness than alloy B due to high fraction of eutectics in intergrain areas. Age hardening response of alloy B on 150°C is maximum after 15 hours of age-hardening treatment. Peak in age-hardening curve of alloy B is probably caused by maximum volume fraction of fine dispersive particles (type MgZn or MgZn<sub>2</sub>) in  $\alpha$ -Mg matrix (Fig. 8), however detailed investigation of this assumption by means of transmission electron microscopy has not yet been carried out. Later decrease of hardness of alloy B may be caused by time

dependent coarsening of dispersive precipitates. But this conclusion has been made only with consideration of solid solution micro hardness time dependence of alloy B as seen on Fig. 7a.

Age-hardening temperature of alloy A (150°C) is probably insufficient; lack of distinct maximum in age-hardening curve and also slight and unfinished increase of hardness with time of hardening in Fig. 7a implies, that peak of hardness may be achieved after 1000 or more hours of age-hardening. Therefore, choice of higher age-hardening temperature will be inevitable.

#### 4. Summary

- Microstructure of both alloys consists of cells of solid solution and intercellular eutectics phases or other massive phases. Cell size and area fraction of intercellular phases is in both alloys approximately similar.
- Eutectics of alloy A is formed by lamellae of cubic W -  $\text{Mg}_3\text{Zn}_3\text{Y}_2$  phase and lamellae of solid solution  $\alpha$ -Mg. Eutectics of alloy B is formed by lamellae of icosahedral I -  $\text{Mg}_3\text{Zn}_6\text{Y}$  phase and lamellae of solid solution  $\alpha$ -Mg. Both I and W phases were in the structure of alloys found also in separate massive form.
- Massive phase rich on Nd occupies intercellular areas and is independent on Zn:Y relation in both alloys.
- Hardness of alloy A slightly increases with time of ageing, however maximum of ageing response is not significant. Hardness of alloy B reaches maximum after approximately 15 hours. Hardness growth is about 15 HV. After over ageing occurred slight decrease in hardness.
- Hardening in both alloys is probably caused by precipitation of fine dispersive particles in  $\alpha$ -Mg matrix oriented in  $[0001]_{\alpha\text{-Mg}}$  direction.

#### Acknowledgment

*Author gratefully acknowledges the financial support by Czech Science Foundation (project 106/06/0252).*

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