ARCHIVES OF METALLURGY

Volume 45 2000 Issue 1

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THE INFLUENCE OF INTERGRANULAR MICROSTUCTURE OF Mg-Zn-RE ALLOYS ON PROPERTIES AT ELEVATED TEMPERATURES

WPŁYW ODLEWNICZEJ STRUKTURY STOPÓW Mg-Zn-RE NA WŁASNOŚCI W PODWYŻSZONYCH TEMPERATURACH

Two magnesium-alloys with small amounts of zinc and rare earths were investigated in order to compare the influence of cast structure and heat treatment on hardness and tensile properties. The structure has been examined using the methods of scanning and electron microscopy; tensile tests were carried out at temperatures from ambient up to 300°C. It was established that the structure of the alloys consists of fine equiaxial grains of solid solution of Zn, and RE in Mg surrounded with a network of the ternary eutectic of Mg_{12}(RE, Zn) or $Mg_{12-x}Zn_xRE$ type, which is hard and brittle. The eutectic is responsible for stability of mechanical properties of the alloys at elevated temperatures up to 200°C. They also reveal small response to heat treatment, which make them cheaper to produce than other alloys like ZE 41 or EZ 33 and suitable for High Pressure Die Casting (HPDC).

W pracy badano wpływ struktury odlewniczej i obróbki cieplnej na twardość i własności wytrzymałościowe dwóch stopów magnezowych z metalami ziem rzadkich różniących się zawartością cynku. Strukturę obserwowano stosując metody mikroskopii elektronowej, a własności mechaniczne wyznaczano na podstawie próby rozciągania w temperaturach do 300°C. Stwierdzono, że struktura badanych stopów składa się z drobnych, równoosiowych ziarn roztworu stałego Zn i RE otoczonego twardą i kruchą siatką potrójnej eutektyki typu Mg_{12}(RE, Zn) lub $Mg_{12-x}Zn_xRE$. Eutektyka ta jest odpowiedzialna za stabilność własności mechanicznych w podwyższonych temperaturach do 200°C. Stopy te nie wymagają obróbki cieplnej i dlatego ich produkcja jest tańsza niż innych stopów tego typu, jak ZE 41 czy EZ 33. Mogą one znaleźć zastosowanie przy produkcji odlewów metodą wysokociśnieniową (High Pressure Die Casting — HPDC).

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1. Introduction

A number of commercial magnesium casting alloys based on Mg-Zn binary alloy system contains some additions of rare earths metals. The rare earth elements are usually added in the form of mischmetal to reduce costs of production. They are also enriched in small amounts of zirconium in order to refine grain and traces of manganese to suppress corrosion. Such alloys are light, have high strength, good damping properties and corrosion resistance. All the alloys contain a network of eutectic with rare earths responsible for resistance to creep at elevated temperatures. Such properties suggest that they are suitable to applications like engine housings or gear boxes and other parts of aircrafts, where stability of strength properties at elevated temperatures of work is important [1, 2].

One of such aloys is ZE 41 (3.5—5.0% Zn, 0.75—1.75 wt% RE and 0.4—1.0% Zr produced by conventional sand casting; and having good strength and casting properties [3]. Another alloy with good castability and creep properties up to 250°C is EZ 33 (2—3% Zn, 0.4—1.0% Zr, 2.5—4.0% RE), with tensile ultimate stress 16.7 kg/mm^2, and 34.7 kg/mm^2 in compressive test), 0.1 proof stress 9.5 kg/mm^2 and 10, respectively [2]. They are applied after a precipitation heat treatment. Quite recently a new Mg alloy is being designed by Magnesium Elektron called MEZ with 0.35% Zn, 0.3% Mn, 2.5% RE and trace level Zr which is to be produced for High Pressure Die Casting (HPDC) and used without heat treatment for the elevated temperatures applications [4].

The aim of the work has been to examine the influence of rare earths additions on structure, and mechanical properties of the MEZ alloy compared with a binary MgZn 2 wt% one.

2. Experimental

The alloys for experiments were produced from magnesium and zinc of commercial purity following the conventional method of melting and casting magnesium alloys under a protective layer of salts. Zirconium and cerium mischmetal were added as master alloys. The binary MgZn 2 and MEZ 2 (with 2% zinc) alloys were taken as alloys of reference to the MEZ one with 0.35% Zn. The RE mischmetal contained in the MEZ alloys consisted of light rare earths: Ce, La, Pr and Nd and was used in order to reduce costs. The alloys were examined in as cast condition. Specimens for scanning and optical microscopy were mechanically polished followed by etching with solution of either HNO_3 or H_3PO_4 in ethanol. The structure and the phase composition of the alloys were investigated using SEM (SE and BSE) + EDS (Link ISIS). The concentrations of particular elements were evaluated using the internal software ZAF-4. Hardness was measured on cast specimens using Vickers tester at 5 kg load. The examinations of strength properties at ambient and elevated temperatures were carried out in Instron testing machine on series of 5 specimens at room temperature, 100, 150, 200, 250 and 300°C, and fractures modes were studied on longitudinal sections and fracture surfaces. Corrosion was assessed according to ASTMB-11790 standards in 5% NaCl during 1000 hrs at 35°C. The surface area of specimens was 62 cm^2. They were washed in acetone, dried in air and weighed before the test in a Huber's chamber. After the test the corrosion products were removed in water solution of 100 g of $(NH)_2CrO_4$ per 1 l, at ph 10 at ambient temperature. The rate of corrosion was calculated following the equation given in paper [5].

3. Results

3.1. Influence of morphology on fracture mode

The longitudinal sections and fracture surfaces of two Mg alloys in the cast condition; a binary one with 2 wt% Zn and MEZ with 0.35 wt% Zn, 0.3% Mn, 2.5% RE and 0.3% Zr, are shown in Fig. 1 after tensile tests at room temperature.

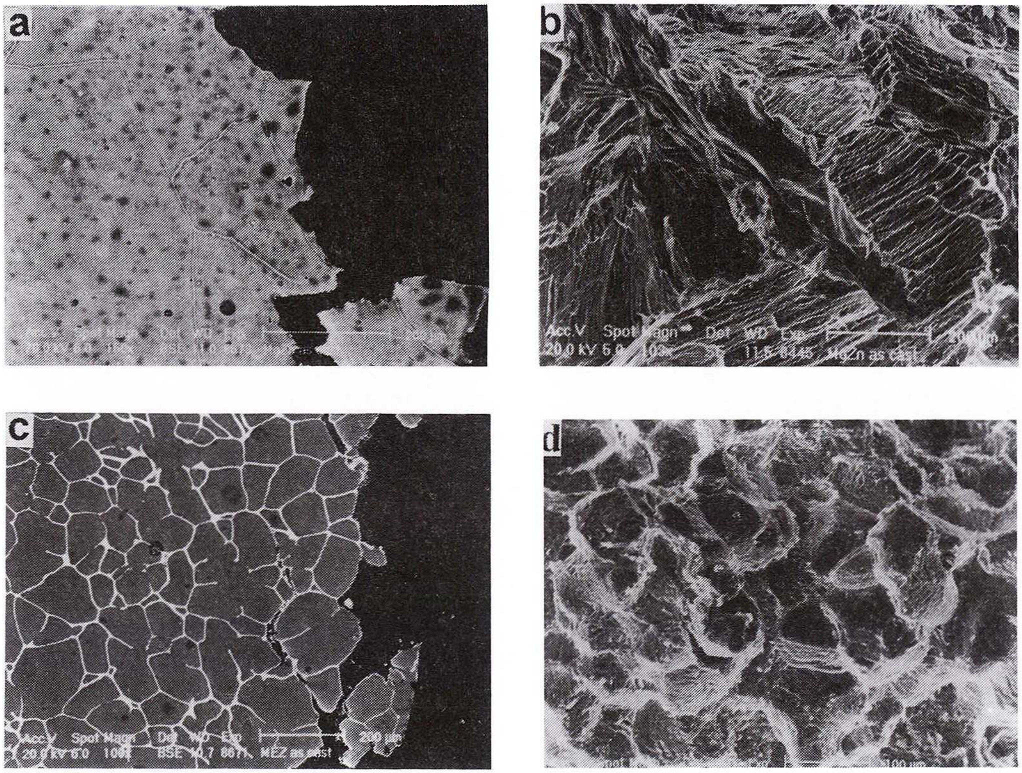

Fig. 1. Micrographs of cast tensile specimens tested at room temperature: a) BSE image of a longitudinal section of Mg-2wt% Zn alloy and b) the SE image o its fracture; c) BSE image of a longitudinal section of MEZ alloy and d) the SE image of its fracture

The binary alloy is built of large (more than 500 µm) dendritic grains of the (Mg) solid solution free from visible precipitates of a second phase (Fig. 1a). After alloying it with RE, zirconium and manganese the structure becomes fine with almost equiaxial grains, several times smaller than in the binary alloy (Fig. 1c). A network of eutectic along which failure occurs (Fig. 1c and d), surrounds them quite tightly. The transgranular mode of fracture observed in the binary alloy changes into intergranular in the MEZ alloy. In Fig. 1b a fluted surface, which shows planes of cracking as well as cleavages, can be seen in the MgZn2 alloy.

3.2. Identification of the second phase

The EDS analysis was carried out to determine the composition of the eutectic in the MEZ alloy. An extrapolation technique [6] enabled us to eliminate the influence of Mg-matrix on the EDS results and to estimate the composition of the second phase to be mostly $M_{12}Ce$ type with zinc that substitutes part of RE or Mg. More precise analysis showed that RE elements appear in the eutectic in somewhat various mutual ratios. The SE micrograph of the eutectic together with the EDS results are shown in Fig. 2, where the amounts of the chemical constituents of the eutectic are plotted relative to the magnesium atomic concentration.

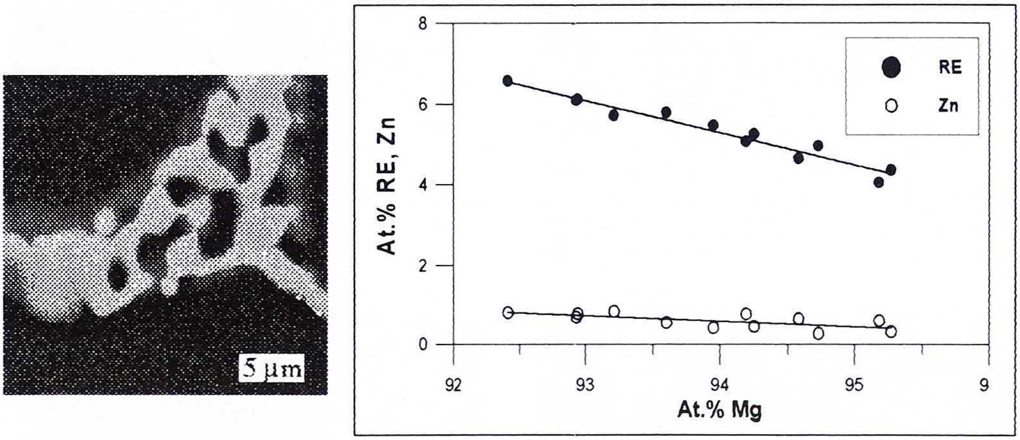

Fig. 2. The SE micrograph of the eutectic in the MEZ alloy together with the variation of RE and Zn concentrations versus Mg concentration in the eutectic

All the rare earth metals are considered as one addition for simplification of estimations. Such a procedure seems to be justified as all of them (La, Ce, Pr and Nd) have similar atomic structure and weight, dissolve in magnesium in limited amounts and form eutectic of ($Mg + Mg_{12}RE$) up to about 7.69 at% (La, Ce) in the alloy without zinc [7]. Since the phase is reported to be nonstoichiometric some precipitates of a lower ratio of magnesium to RE showed in Fig. 3 might also represent the same phase according to the formula $Mg_{12-x}Zn_xRE$. Based on the extrapolation technique they might as well be Mg_9(RE, Zn) phase according to reports of Rohlin [8], or $Mg_{8,25}$RE as was obtained in X-ray analysis for the alloy with 2 wt% Zn which suggests that in the presence of zinc the solid solubility of rare earths in magnesium increases. In most analysed precipitates zinc accompanied RE. An example of an EDS analysis performed in step by step mode across a grain of the MEZ alloy is shown in Fig. 3.

3.3. The mechanical properties

The tensile tests showed that strength of the cast alloys depended not only on the amount of RE but also on the amount of zinc (table). Thas is why the binary MgZn2 alloy reveal $R_m = 140$ MPa, which is close to that for the MEZ 2 (with 2% Zn), consistently with observations of Emley [2] and Lagowski [9] who reported the hardening effect of zinc on magnesium up to 10 wt% of zinc. The higher values of R_e and HV in the MEZ alloy suggest that its strengthening results from RE additions (apart from influence of Zr on grain size). The lower tensile strength of the MEZ may be due to the change of fracture mode from transgranular in the binary alloy into intergranular in the MEZ one. It is not surprising then, that the elongation was the smallest in the MEZ alloy. The microhardness measurements proved that the eutectics was twice as hard (203 HV) as the solid solution of Zn, Zr and Mn in magnesium, which was quite ductile (see dimples in Fig. 1d).

TABLE

The mechanical and tensile properties of the cast Mg-Zn alloys

Alloy	Tensile strength R_m [MPa]	Proof strength R_e [MPa]	Elongation A_5 [%]	Hardness HV_5
Mg-Zn 2 wt%	140	40	12	50
MEZ	130	55	3.5	60
MEZ 2	150	67	6	70

Neither heat treatment nor ageing induced any change of the mode of the fracture, which propagates along the eutectic. The structure proved to be resistant to precipitation hardening, as hardness of the alloy increased only by 12HV after 30 hrs at 200 or 240°C reaching only the value it had prior to the heat treatment (500°C/6hrs). No metastable precipitates were observed in thin foils in TEM apart from the large eutectic ones of Mg_{12}RE type. This is different from the ZE 41, EZ 33 or QE 22 alloys, where fine precipitates of the β phase hardened the alloy at ageing [2, 10]. The reason is that the amount of zinc has been probably too little or tied up in the eutectic precipitates with RE leaving only about 0.2 wt% in the solid solution (Fig. 3).

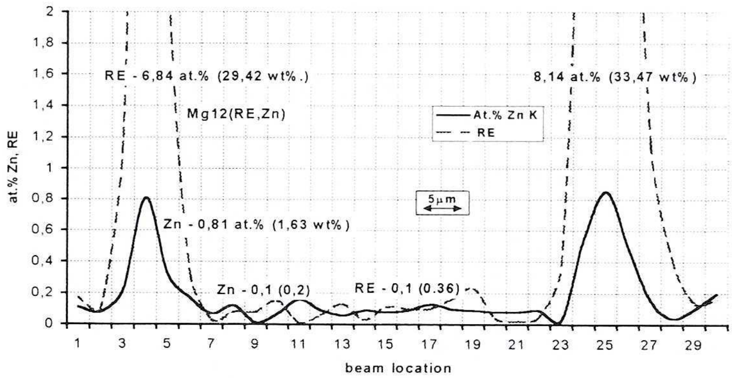

Fig. 3. The EDS distribution of Zn and RE across the grain of the cast MEZ alloy. (The changes of Mg content, Mn and Zr that enter merely the Mg-solid solution are omitted here for sake of clarity)

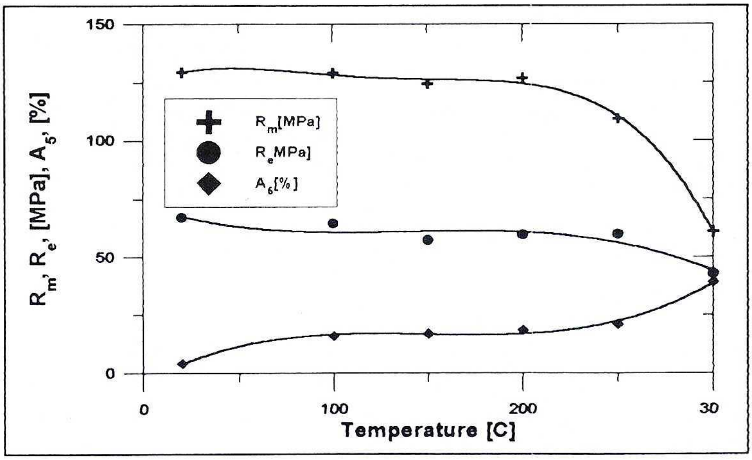

Fig. 4. The strength properties of the MEZ alloy at elevated temperatures

The results of tensile tests carried out at elevated temperatures on MEZ specimens are shown in Fig. 4. It can be seen that the alloy properties are stable up to 200—250°C and then the tensile strength and proof strength fall rapidly, while the elongation increases. Above 250°C, the plastic deformation starts, eutectic cracks, and fracture occurs with formation of a neck (Fig. 5a, b). The deep dimples visible in Fig. 5b are a good illustration of the behaviour. The structure of the MEZ 2 alloy (with 2 wt% Zn) remains stable at elevated temperatures up to 200°C and fracture proceeds in the same way. Although the strength properties of the alloy are higher: $R_m = 150$ MPa, $R_e = 70$ MPa due to higher amount of zinc, both alloys behave alike when strained at elevated temperature, which proves that rare earths (forming stable eutectics) are responsible for preventing their strength at elevated temperatures, while zinc hardens the solid solutions of the cast alloys.

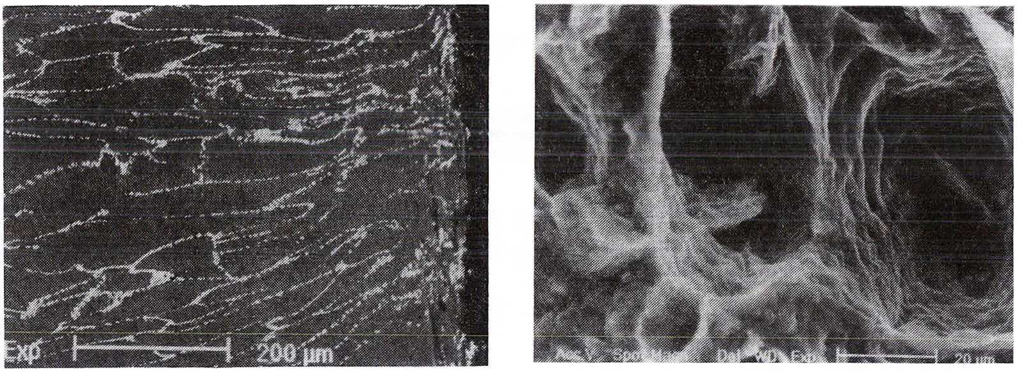

Fig. 5. The SE micrographs of the MEZ alloy fractured at 300° C: a) longitudinal section, b) fracture surface

3.4. Corrosion resistance

General service conditions for magnesium alloys are at temperatures where direct oxidation does not play a significant role. Hence, the corrosion behaviour in salt containing environment is more important for evaluation of magnesium alloys than in others.

The results of standard salt water spray corrosion test carried out for the binary and both MEZ alloys are shown in Fig. 6.

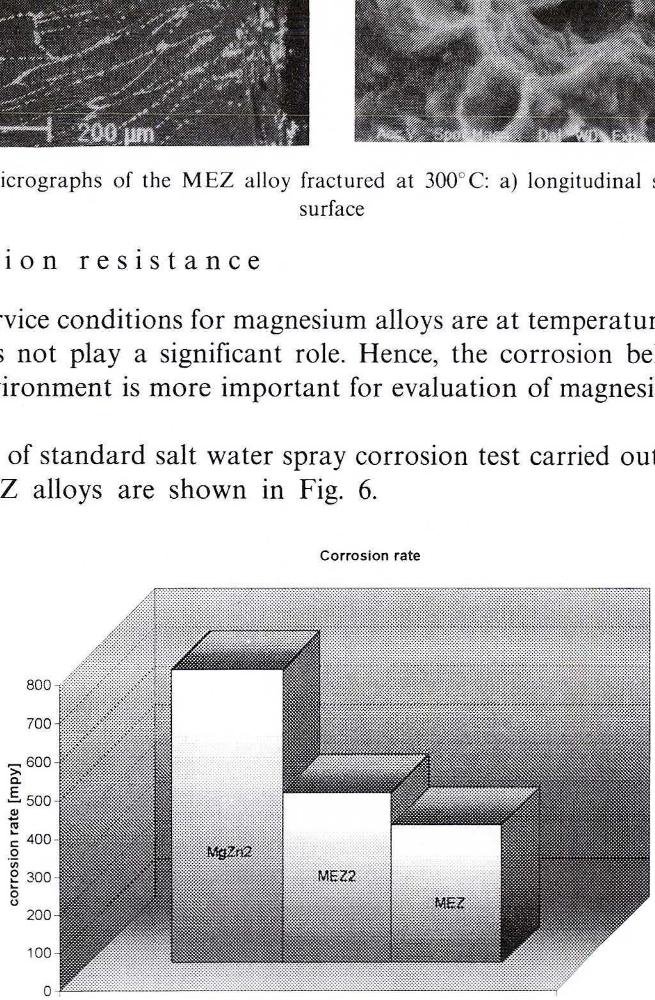

Fig. 6. The average corrosion rates of Mg-Zn alloys in salt water after 1000 hrs

The weight loss WL (in mg) was used to determine the average rate of corrosion (v) over the test period in mils (thousands of an inch) per year {mpy} according to the following equation:

$$v = \frac{WL}{E \times A \times D} 143.7 \text{ [mpy]},$$

where:

E — the exposure time in days,
A — the total surface area in cm^2,
D — the density of material g/cm^3, which was $1.74\,g/cm^3$,
143.7 — conversion constant.

The results of corrosion test show that the alloys exhibit little corrosion resistance in salt water. The surface of the specimens was covered with deep caverns. The weight loss was considerable. However, the MEZ alloy was the most corrosion resistant of the three investigated ones, while the binary MgZn2 was the worst. Since the two MEZ alloys differ merely by the zinc amount, it must be it, which is responsible for the increase of corrosion in the MEZ alloy with higher addition of Zn. The corrosion rate was apparently almost twice suppressed, not only by addition of manganese to the binary alloy, but also by grain refining effect of zirconium [5]. The structural observations of the cross-sections proved that the corrosion is of surface type and does not propagate along the eutectic network.

4. Conclusions

Based on the investigations carried out in the work, it follows that:

— the dendritic, coarse structure of the Mg-Zn alloy transforms into a fine one in MEZ alloys with a network of the ternary eutectic of $Mg_{12}(RE, Zn)$ or $Mg_{12-x}Zn_xRE$ type,

— the solid solution of zinc in magnesium is ductile. It also reveals considerable elongation, which decreases after alloying with the RE mischmetal due to the appearance of the ternary eutectic, which is hard and brittle,

— the fracture mode during tensile test of the investigated alloys changes from transgranular in the binary alloys into intergranular type in the MEZ alloys affecting the tensile strength of the MEZ alloys,

— the response to ageing processes of the MEZ alloys seems to be negligible, and the strength and plastic properties of the alloys investigated remain stable at elevated temperatures due to the presence of the ternary eutectics. Above the critical temperature the plastic deformation begins in the specimens and the eutectics cracks into pieces, while ductile solid solutions extend and the fracture occurs with formation of a neck.

Acknowledgements

This work was supported by the Polish State Committee for Scientific Research under Research Projects No 7 T08 B018 09 and No 7 T08 B045 12.

The authors are grateful to MEL Magnesium Elektron, Manchester for supplying the alloys and their components for investigations.

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REVIEWED BY: PROF. DR HAB. INŻ. ANDRZEJ PAWŁOWSKI

Received: 12 September 1999.