Effect of the Porosity Range and its Nature on Mechanical Properties of Magnesium Alloys Mg-Al-Zn

M.B. Ismailov*, Zh.M. Ramazanova, G.B. Nigmetchanova, S. Tolendyuly, L.M. Mustafa

JCS "National Center of Space Research and Technology", str. Shevchenko, 15, 050010, Almaty, Kazakhstan

Article info

Received:
21 July 2015

Received and revised form:
27 September 2015

Accepted:
23 October 2015

Keywords:
magnesium alloys,
porosity, tensile strength,
yield strength, elongation.

Abstract

The possibilities of porosity adjustment in alloys of the Mg-Al-Zn system obtained by melting under a layer of flux were studied. The elements that significantly increase corrosion resistance and heat resistance, and improve mechanical strength and technological characteristics were chosen as doping components. Measurements showed that the range of porosity varied between 5.9 and 14.8%, and the relationship between porosity and strength of alloys was defined for the first time for this range. For an alloy with porosity of 14.8%, the percentage of open pores was 12.8% while the percentage of closed pores was 2%. Micro-hardness of alloys with the given porosity was 661 MPa after casting, 876 MPa after homogenizing annealing and 897 MPa after artificial aging. The tensile strength was 235 MPa. Analysis identified that the main cause of porosity was catching atoms of hydrogen from atmosphere by molten alloys during melting, casting and liquation. In order to reduce the percentage of porosity alloys were doped by metal manganese, liquid metal was processed by calcium and hexachloroethane, and casting form was treated by boron nitride. These manipulations resulted in reduction of samples porosity up to 5.9%, increase of tensile strength up to 240 MPa. Open porosity was 4.5%, while closed porosity was 1.4%. At the same time micro-hardness of cast samples was 867 MPa, 903 MPa after homogenization annealing and 961 MPa after artificial aging. Further reduction of porosity and increasing of magnesium alloys strength is possible with the use of inert gases or vacuum melting. Samples porosity can be increased by more than 14.8% with the help of melting in the hydrogen containing atmosphere.

1. Introduction

Magnesium alloys are widely used as structural materials in aerospace, vehicle and instrumentation manufacturing industries. Unique features of such alloys are high specific mechanical strength, ability to effectively absorb elastic vibrations (damping capacity) and extremely high vibration fatigue strength. These alloys are usually porous. The porosity of the material strongly affects its strength and corrosion resistance. The material has the highest strength and corrosion resistance when its porosity is close to zero, but the melting and casting process in this case is very complex. Magnesium alloy with moderate porosity (relative range is 6–15%) is also in demand; it is cheaper and more available. In this case pores are sealed with impregnating the material with special fluids [1, 2].

The interest to magnesium alloys was recently renewed as to biodegradable materials suitable for making implants in osteosynthesis. It is desirable to use porous materials for bone implants. In this regard, the magnesium alloys have a great potential use, as they are completely biocompatible, possess mechanical properties of a natural bone, do not cause any inflammatory response and stimulate the growth of new tissue [3, 4]. However, it is still difficult to obtain magnesium alloys with high porosity up to 75%, exceptionally with open pores [5]. The sizes of micro pores in magnesium alloys are ranged from 100 to 500 μm [6]. At the moment they are presented with several magnesium alloys with bio-corrosion and mechanical properties in the market: ML-5 and ML-10 in the Russian industry, and AZ91A, AZ91B, AZ91C, AZ91D, AZ91E, LAE442 in the world market [7]. It is established that

* Corresponding author. E-mail: m.ismailov@spaceres.kz

magnesium alloys have good biocompatibility, corrosion resistance and have Young's modulus, which is close to the modulus of cortical bone [8]. One of the methods to obtain porous materials is the method of directional solidification of the melted metal with the saturated gas. This method is also called the method of gas-eutectic reaction or Gazar process [9].

The dependence of the porosity and strength of magnesium alloy from specific melting and casting processes needs further study and optimization. Knowledge of these processes is important for creation of a family of alloys different under the "price and quality" criterion.

The purpose of the work is to study the possibility of obtaining magnesium alloys of the Mg-Al-Zn system with various porosity ranges.

A well-known casting magnesium alloy of the Mg-Al-Zn system that is chemically identical to ML5 and its European analogue AZ91E was experimentally studied. The chemical composition and the strength characteristics are given in Table 1.

Al and Zn as alloying elements of the alloy act as reinforcing additives, and Mn improves the corrosion resistance. Manufacture of magnesium alloys of the Mg-Al-Zn system with different range of porosity was carried out according to two schemes.

Scheme 1. The material was melted at 720 °C during 10 min. Alloying additives, such as aluminum, zinc, manganese, were added into the melted material as pure metal with melting under a layer of the VI2 protective flux. The melted material was refined at 720 °C of the melted material by its mixing with a stirrer made of heat-resistant steel within 5 min and with adding of the VI3 dried flux. The alloy was modified by overheating at 750 °C for 15 min until the carbon dioxide bubbling on the surface of the melted material stopped. The melted material was held for 10 min with the temperature decrease up to 740 °C, and used for molding with the help of a graphite mold. The process was accompanied with purging the casting melted material jet with the VI3 finely ground flux. Homogenization annealing of the casting samples was done at 420 °C within 10 h followed with quenching in air. Artificial aging was carried out at 190 °C for 12 h with air cooling.

Scheme 2. It differs from the Scheme 1 with the use of additional activities to be added to reduce the content of the dissolved gas in the melted material:

- anticorrosion addition of Mn into the melted material was added with the help of the AlMn ligature, because the metal Mn is very hardly soluble in the melted magnesium;
- after refining an additional degassing operation was introduced: the temperature of the melted material was increased up to 750–780 °C, then metallic Ca in the amount of 0.1% and hexachloroethane in the amount of 0.2% by weight were sequentially added into the melted material with the help of a special device in the form of a bell, the process took up to 10 min;
- before pouring of the melted material the graphite molds were treated with an alcoholic solution of boron nitride and annealed.

2. Research Methods

The microstructure of the alloy was analyzed with a microscope Axiovert 200 MAT with use of such methods as quantitative metallography and by comparing the structure with the help of known scales. A sample preparation complex BRILLANT 221 was used to grind the samples taking into account all the characteristics to prepare metal alloy samples to study structural compositions. X-ray phase analysis was made with the help of a diffractometer D8 Advance (BRUKER), and radiation α-Cu. Mechanical properties of the material were determined with the help of a tensile testing machine Shimadzu with further computer processing. Cross section samples were used to test the mechanical properties. The samples were stretched at the room temperature with the speed of 0.5 mm/min. Micro porosity was determined with the help of an optical microscope, by calculating the area of the pores in the photographs using the method developed by S.A. Saltykov [10]. Micro porosity was also determined gravimetrically, by immersing

Table 1
Chemical Composition and Strength of Standard Casting Magnesium Alloys

Alloy	Chemical Composition, % Weight				Tensile Strength UTS, MPa
	Al	Zn	Mn	Mg	
ML5	7.5-9.0	0.2-0.8	0.15-0.5	89.7-92.15	235
European Analogue of AZ91E Alloy	8.7	0.7	0.17	90.43	240

a sample into water. The third method of measuring the amount of micro porosity was done with the help of the analyzer KATAKON Sorbtometer M, where liquid nitrogen was used as an adsorbent.

3. Results and Discussion

The method to obtain a magnesium alloy of the Mg-Al-Zn system under flux according to Scheme 1 enabled us to obtain the alloy with a chemical composition in wt.%: Al – 8.3; Zn – 0.56; Mn – 0.013; Mg – the rest. The chemical composition of the alloy obtained corresponded to the composition of the commercial alloys (Table 1), except for manganese the content of which was significantly lower. Metallographic researches showed that casting samples had a dendrite structure and homogenization annealing allowed a transition to a crystalline structure with grain sizes of 13–15 μm, after aging the grain size was reduced up to 10–11 μm. XRD analysis (Fig. 1) showed that the system Mg-Al-Zn consists of grains of α-solid solution of magnesium-based binary eutectic and non-equilibrium $\alpha + \gamma$ ($Mg_{17}Al_{12}$), which occur due to degeneracy of inclusions represented non equilibrium γ-phase ($Mg_{17}Al_{12}$). Intermetallic phase γ ($Mg_{17}Al_{12}$) was released as light impurities at the grain boundaries and dendrite cells of α-solid solution, which is showed in Fig. 2. Zinc does not form intermediate phases in alloy, it is dissolved in magnesium and partly included in the phase γ $(Mg, Zn)_{17}(Al, Zn)_{12}$.

When studying the microstructure of the alloy obtained in the pictures it can be seen many micro pores as dark spots. Results of final analyses of micro porosity of the alloys showed that the total porosity was 14.8%, and this value was too high for structural alloys. Porosity was structurally composed from 12.8% of open pores and 2% of closed pores. Not more than 4.4% of the total porosity was formed under the shrinkage mechanism during crystallization of the melted material, and the rest of 10.4% was due to the gas absorption by the melted material.

The micro hardness of the alloy obtained was 661 MPa in the cast state, 876 MPa after homogenizing annealing, 897 MPa after artificial aging process. The strength characteristics of the final sample were UTS = 235 MPa, σ_{02} = 108 MPa, δ = 2.7%.

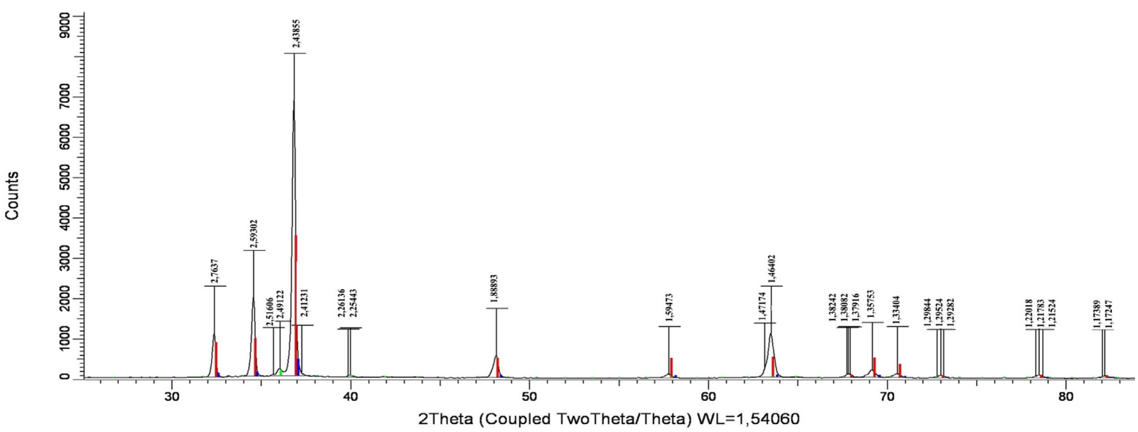

Fig. 1. X-Ray Analysis of the Porous Aluminum-Magnesium Alloy: Solid solution of aluminum in magnesium – 94.74%; γ – $Mg_{17}Al_{12}$ – 5.26%.

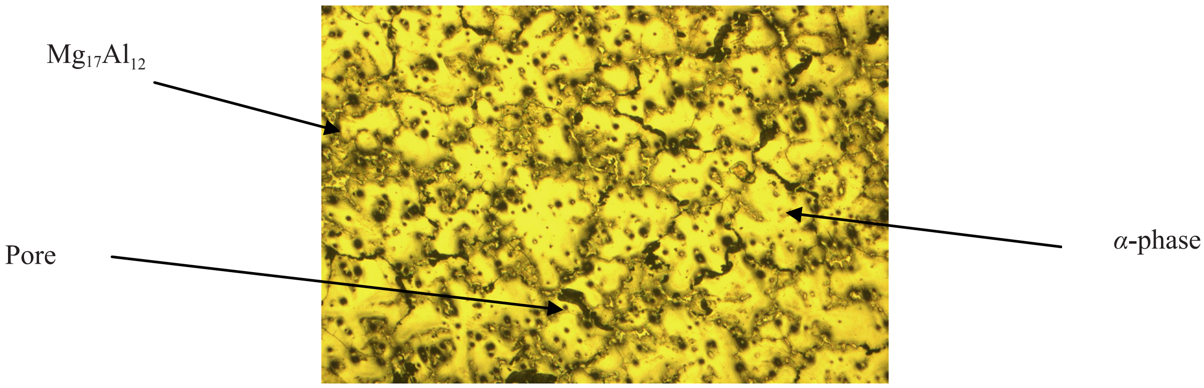

Fig. 2. Microstructure of the Porous Aluminum-Magnesium Alloy, x200.

It is known that micro porosity of magnesium alloys is the natural result of two physical processes occurring during crystallization of liquid alloys, i.e. shrinkage and gas absorption [2]. Any solid phases newly formed during the cooling of the melted material and its crystallization have a higher density resulted in shrinkage porosity of the samples. The second component of the total porosity is gas porosity. Absorbed gases consist of 70% hydrogen [11]. It is known that the atmosphere consists of N_2, O_2, H_2O, CO_2 and other components. Melted magnesium does not dissolve these gases, however, reacts actively with N_2, O_2, H_2O, CO_2, under the following reactions:

$$2Mg + O_2 \rightarrow 2MgO$$

$$3Mg + N_2 \rightarrow Mg_3N_2$$

$$2Mg + CO_2 \rightarrow 2MgO + C$$

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + 2H$$

Among the products of these reactions only atomic hydrogen was actively absorbed by melted magnesium. This process went with heat absorption and decrease of the temperature of the melted material. Furthermore, the solubility of atomic hydrogen decreased as a result of the melted material crystallization. The excess of hydrogen began to separate with bubbles in the melted material. Then micro pores were appeared in the place of gas bubbles.

Experiments according to Scheme 2 had the following results. Chemical composition of the samples corresponded to wt.% as follows: Al – 7.44, Zn – 0.48, Mn – 0.454; Mg – the rest. The total porosity was 5.9%, including closed (1.4%) pores and open ones (4.5%).

The micro hardness of cast samples was 867 MPa, and 903 MPa after homogenization annealing, 961 MPa after artificial aging. This is 7% higher than the values of the porous samples prepared according to Scheme 1. The strength characteristics of the final samples were: UTS = 240 MPa, σ_{02} = 110 MPa, δ = 4.2 %. These data corresponded to the characteristics of the industrial samples of the alloys of the Mg-Al-Zn system shown in Table 1.

The relationship curve of the strength of the magnesium alloy ML5 (AZ91E) on a range of porosity up to 15% was made (Fig. 3) according to the characteristics of samples manufactured under Schemes 1 and 2 and the strength characteristics of the low porous samples [6, 12].

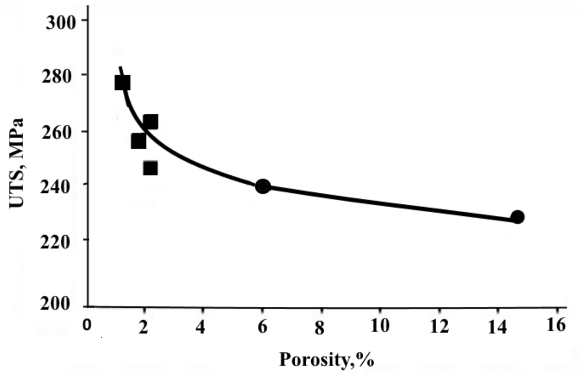

Fig. 3. Relationship between Tensile Strength and Porosity of Magnesium Alloys: ML5 (AZ91E), where ■ – under the data from [6, 12], ● – under the authors' data.

Both curves obtained for small values of porosity, have sharper relationship, and when the porosity is higher than 4% they become flatter, and the influence on the strength decreases. This relationship is important because it allows estimating the strength of the alloy under the known value of porosity. As it is seen in Fig. 3, to achieve high strength of alloys the porosity of an alloy should be less than 4%. To obtain magnesium alloys with strength characteristics of more than 260 MPa it is necessary to reduce the porosity up to 1–3%. Vacuum melting methods can be used to achieve this but with greater complication of the production process and increase of the alloy cost.

It is clear that porosity increase of magnesium alloys for more than 15% with open pores can be achieved by reducing the coating flux and adding of hydrogen to melting pot. This is a topic for the further studies.

4. Conclusions

Depending on condition, the micro-hardness of alloys with 12.5–12.8% of porosity was 661 MPa, 876 MPa and 897 MPa after casting, homogenizing annealing and aging respectively. Tensile strength of porous alloy was around 235 MPa. After manipulations to reduce the porosity to 4.5% the mechanical characteristics, especially micro-hardness reached following: 867 MPa after casting, 903 MPa after homogenization annealing and final operation allowed having 961 MPa.

Alloys of the Mg-Al-Zn system with the porosity up to 6%, with the strength characteristics corresponding to commercial alloys ML5 (AZ91E) can be prepared according to Process Scheme 2. To improve the performance of the material it is impregnated with special anti-corrosive liquids sealing open pores.

Alloys of the Mg-Al-Zn with porosity up to 15% can be obtained according to Scheme 1. The pores are open. The alloy is relatively cheap and applicable as a structural material after impregnation with sealing liquids.

Magnesium alloys with a high rate of open porosity (75%) are used as biodegradable implants. Currently, there is an intensive search for effective technologies to produce such materials. Results of this work showed that the open porosity of the magnesium alloy may be increased with melting in the atmosphere containing hydrogen.

Magnesium alloys with low porosity (less than 4–6%) are the strongest; they are used as structural materials. The optimal technology for their production is vacuum melting or melting in an inert gas.

References

[1]. A.A. Donskoj. Aviation Industry Sealants [Klei. Germetiki. Tehnologii] = Glues. Sealants. Technologies 2 (2005) 14–27 (in Russian).

[2]. Z.P. Uridija, I.Yu. Mukhina. New Impregnating Materials for Sealing of Magnesium and Aluminum Alloys Casting. [Vse materialy. Ehnceklopedicheskij spravochnik] = All materials. Encyclopedic Reference Book. 2011. 8, 10 (in Russian).

[3]. M.P. Staiger, A.M. Pietak, J. Huadmai, G. Dias, Biomaterials 27 (2006) 1728–1734.

[4]. C. Lorenz, G.J. Brunner, and P. Kollmannsberger, Acta Biomaterialia 5 (2009) 2783–2789.

[5]. I. Morgenthal, O. Andersen, C. Kostmann, G. Stephani, T. Studnitzky, F. Witte and B. Kieback. Adv. Eng. Mater. 16 (3) (2014) 309–318.

[6]. Liang Wang, Hongjoo Rhee, Sergio D. Felicelli, Adrian S. Sabau, John T. Berry, Oxide Film and Porosity Defects in Magnesium Alloy AZ91. Shape Casting: 3rd Intern. Symp. 2009, p. 348.

[7]. M.L. Grokhova, I.F. Belenichev, V.N. Cherny, Y.V. Yatsun, Research of Toxical Effects of Biodegradation of Modified Magnesium Based Alloy ML-10 on Laboratory Rodent's Organism// online version - http://www.sworld.com.ua/index.php/ru/conference/the-content-of-conferences/archives-of-individual-conferences/march-2013/ (submission date 30.03.2015).

[8]. V.M. Chernyj. Prospectives of Use of Biodegradable Magnesium-based Alloys in Osteosynthesis [Zaporozhskij meditsinskij zhurnal] = Zaporozhye Medical Journal. 2013. 6, 76-79 (in Russian).

[9]. V.Yu. Karpov, O.V. Komissarchuk. Structure and Mechanical Properties of Porous Aluminum Alloys Obtained by Directional Solidification - http://www.metaljournal.com.ua/ (submission date - 03/30/2015) (in Russian).

[10]. S.A. Saltykov. Stereometric Metallography M.: [Metallurgiya] = M.: Metallurgy. 1970. 375 (in Russian).

[11]. B.J. Zhang, J.G. Shan, J.L. Ren, P. Wen, Welding journal 92 (4) (2013) 101-s to 109-s.

[12]. N. Moscovitch, G. Gertsberg, N. Nagar, M. Lautzker, N. Fantetti and B. Bronfin, The Effect of Porosity on the Microstructure and Mechanical Properties of Die-cast Mg Alloys: SAE 2006 World Congress & Exhibition Technical Session Schedule, 2006.