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Research Article

Corrosion behavior of heat treated Mg-xZn (x=0.5 – 3) alloys

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Abstract

The purpose of this study is to investigate the effects of zinc (0,5-1-2-3 wt.%) additions and heat treatment parameters on the microstructure, hardness and corrosion properties of magnesium zinc alloys. After the solution heat treatment at 400°C, the samples subjected to 8 and 16 hours heat treatment. Microstructure studies showed that the grain size decreased with the increase of Zn content and the MgZn intermetallic phase was formed by the addition of 3 wt.% Zn. Hardness of the samples was increased with increase of Zn content before and after heat treatment. For the as-cast samples, as the amount of Zn increased, corrosion current density (I_{corr}) and corrosion rate (P_i) increased. As the amount of Zn increased, I_{corr} and P_i values decreased after 8 hours and 16 hours of heat treatment respectively. It can be suggested that in the galvanic couple of Mg-3Zn, α -Mg matrix phase behaves as an anode and MgZn intermetallic phase behaves as a cathode.

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1. Introduction

Magnesium and its alloys with good ductility, strength and good corrosion resistance, as well as having low density, are becoming the focus of interest for researchers in the automotive, aerospace and electronics industries [1-3]. Mg with a density of 1.74 gr/cm³, is 36% and 78% lighter than Al and steel respectively and magnesium alloys are the lightest metallic material used today as a construction material [1-5]. However, magnesium alloys which have poor corrosion resistance due to their electrochemically active conditions limit their use especially in aerospace and automotive fields [6]. Mg is a very active metal with an electrochemical standard potential value of -2.37 V at 25 ° C and -1.7 V at 3% NaCl and is used as a sacrificial anode [7]. Important studies have been done to understand the corrosion principles for magnesium and to improve the corrosion resistance through the design and development of new alloys, inhibitor addition, heat treatment and coatings [8-13]. Heat treatment may have a significant effect on the corrosion behavior due to its modifying properties in the microstructure [14]. Zn also increases the hardness, strength and also the fluidity of the alloy at ambient temperatures through the precipitation hardening [15]. Bakhsheshi-Rad et al. [6] reported that heat treatment improved the corrosion resistance of both Mg-3Zn and Mg-6Zn alloys. Xian-bin et al. [10] indicated that compared with as-cast alloy, the amount of MgZn particles decreased by the T4 treatment, and consequently T4 treatment increased the corrosion resistance while the T6 treatment decreased the corrosion resistance of the Mg-3Zn alloy in 0.1 mol/L NaCl solution. Cai et al. [15] studied on Mg-Zn alloys containing 1, 5 and 7 wt.% Zn in simulated body fluid (SBF) suggests that corrosion resistance increased with increasing Zn content in the range 1-5 wt.% despite the presence of the potentially

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detrimental MgZn intermetallic. Excessive addition of Zn over 7 wt.% resulting microgalvanic corrosion acceleration. In addition, a wide variety of magnesium alloys, including magnesium-aluminium-zinc (AZ series) were investigated for in vitro and in vivo conditions for implant applications [16-20]. In this study, systematically it was aimed to investigate the effects of both zinc content and heat treatment on the corrosion behavior of the binary Mg - Zn alloys containing low levels (0.5-1-2 and 3 wt.%) of zinc.

2. Experimental Procedure

High purity magnesium (99.99 wt.%) and zinc (99.999 wt.%) which were purchased from Bilginoglu Industry in Turkey were used to prepare magnesium-zinc binary alloys by melting magnesium in a graphite crucible under argon gas atmosphere at 750°C. In order to prevent losses due to evaporation, the addition of zinc was carried out 1 min. before the casting process. The casting process of the molten alloy was carried out using a shielded CO₂ + 0.8% SF₆ mixed gas into a cast iron mold (preheated to 250 °C) having a length of 20 mm and a length of 200 mm. The chemical compositions of the alloys were analyzed using a chemical analysis method (Spectrolab M8 Optical Emission Spectrometer (OES)) and presented in Table 1. The samples were etched in 5 ml acetic acid, 6 gr picric acid, 10 ml distilled water and 100 ml ethanol and then observed under optical microscope (Nikon MA200) for microstructure analysis. Depending on the nominal zinc content, as-cast Mg-Zn binary alloys were designated as Mg-0.5Zn, Mg-1Zn, Mg-2Zn and Mg-3Zn, respectively.

Table 1. Chemical compositions of the as-cast magnesium-zinc binary alloys.

Alloy	Composition wt.%				
	Zn	Mn	Fe	Cu	Mg
Mg-0.5Zn	0.56	0.003	0.004	0.0002	Balance
Mg-1Zn	1.08	0.004	0.002	0.0004	
Mg-2Zn	2.11	0.002	0.003	0.0003	
Mg-3Zn	3.12	0.003	0.004	0.0003	

Hardness measurements were performed using a Vickers Hardness tester (Model Shimadzu HMV2) with a steel ball indenter of 2.5 mm in diameter under the load of 5N and maintained for 10s. Hardness values were also determined by taking averages of 5 different values.

Heat treatments were carried out for 24 hours at 400°C for homogenization (T4) and were treated at 200 °C for 8h and 16 h (T6) for ageing treatment. Initially, the samples were placed in the furnace and heated slowly to 400 °C with a heating rate of 3°C / min. Samples were taken from the furnace after 24 hours and then quenched into hot water at about 60°C. After homogenization treatment, cast samples were treated at 200 °C for 8h and 16 h respectively, and then cooled at room temperature.

The electrochemical corrosion test was done using a potentiostat (Model VersaSTAT 3) Electrochemical corrosion experiments were performed at room temperature in a glass cell containing 3.5 wt.% NaCl solution using a standard three-electrode configuration: graphite rod as a counter-electrode, a saturated calomel electrode as a reference electrode and the sample (2.26 cm² exposed area) as a working electrode. Potentiodynamic polarization curves were generated by sweeping the potential from cathodic to anodic direction at a scan rate of 1 mV s⁻¹, starting from -0.50 V up to 0.50 V, versus OCP. Corrosion potential (E_{corr}), corrosion current density (I_{corr}) were calculated by extrapolation from Tafel curves using DC corrosion software. I_{corr} (mA/cm²) is related to the corrosion rate, P_i (mm/year) using [21]:

$$P_i = 22.85 \times I_{corr} \tag{1}$$

3. Results & Discussion

3.1. Microstructure and hardness properties of the Mg-xZn alloys

The microstructures of the Mg-Zn binary alloys used in the study are shown in Fig. 1. Microstructure studies have shown that the grain boundaries are larger before heat treatment and grain structures are finer after heat treatment. In the literature [22], the maximum solid solubility of Zn in Mg is given 2.5 at. % (i.e. 6.2 wt.%) at the eutectic temperature. The grain size of the alloys decreased with the increasing of zinc content and the MgZn intermetallic phase was formed by the addition of 3 wt.% Zn [10,16,17,23]. Zinc element enriches along grain boundaries to display a network microstructure for both T4 and T6-treated alloy. The grain refinement effect of a solid solute element can also be determined by calculating the grain growth limiting factor (GRF). Zn element has a higher GRF than the Al (4.32) and Y (1.70) GRF values of 5.31 GRF, has a growth-limiting effect, which means that Zn has more efficient growth restriction and better grain refinement efficiency [15].

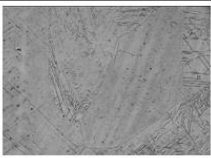

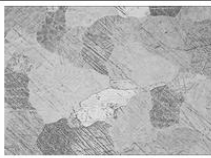
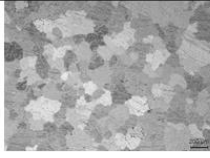

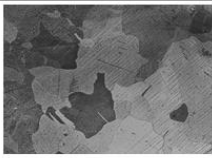
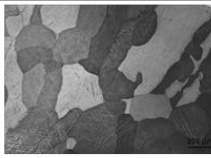
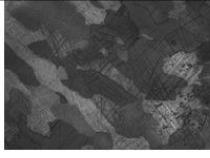
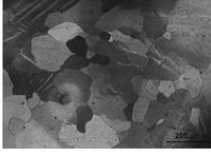
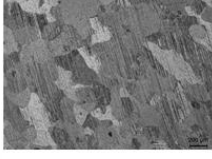
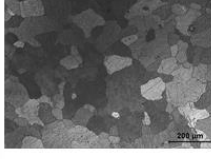
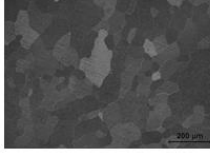
Alloys	Mg-0.5Zn	Mg-1Zn	Mg-2Zn	Mg-3Zn
As-cast				
8h HT				
16h HT				

Fig 1. Optical microstructures of the alloys

In Fig. 2, hardness test results showed that hardness values of magnesium-zinc alloys increased with increasing of Zn content both as-cast and after heat treatments. The improvement of the hardness with the increasing of zinc additions can be explained by the grain refinement. Due to the solidification conditions for the as-cast samples, internal stresses are likely to be inevitable and this may also have caused the hardness to increase. After heat treatment, it is expected that the internal stresses cause relaxation and the hardness of the heat treated samples decreased. Although the grain structures decreased after 8 and 16 hours heat treatment, it was concluded that the Mg-Zn equilibrium diagram in the alloys containing 1 wt.% and 2 wt.% Zn was insufficient to form the hardening.

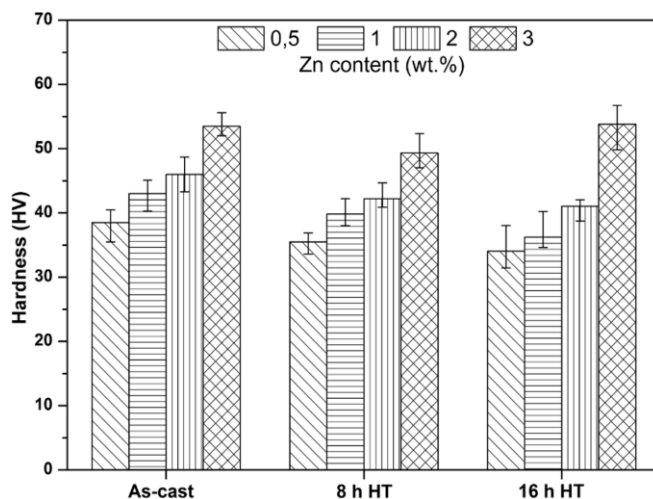


Fig. 2. Hardness values of the alloys

3.2. Electrochemical Corrosion Test

Macrographs, potentiodynamic polarization curves and the electrochemical data obtained from the polarization curves of the as cast and heat-treated samples after electrochemical corrosion tests are given in Fig.3, Fig.4 and Table 2, respectively. Macrographs of the samples after electrochemical corrosion tests are shown that in the as cast samples as the amount of Zn increases, the pits appearing on the surface increased. It can be observed that the pits on the surface of the samples after both 8 hours and 16 hours heat treatments decreased comparing with the as cast samples and thus it might be concluded that the corrosion resistance improved. As a result of the potentiodynamic polarization tests, the corrosion rate decreases as the Zn ratio increases.

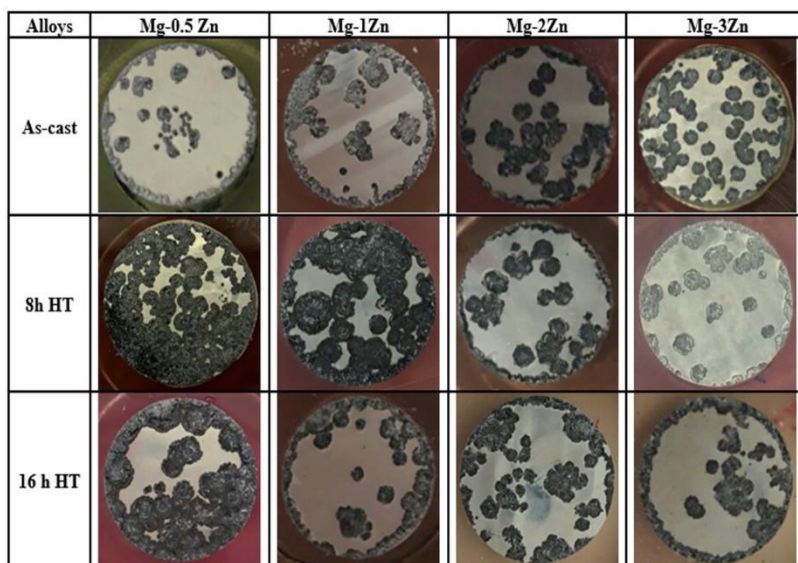


Fig. 3. Macro photographs of the corroded samples after electrochemical test.

The potentiodynamic polarization curves of as cast alloys are shown in Fig. 4. As can be seen, as the amount of Zn increases, corrosion potential (E_{corr}) value of Mg-0.5Zn is more

negative (-1.7 V) than E_{corr} value of Mg-3Zn (-1.65 V) while corrosion current density value (I_{corr}) increased from $18 \mu\text{A}/\text{cm}^2$ in Mg-0.5Zn to $45 \mu\text{A}/\text{cm}^2$ in Mg-3Zn. Corrosion rate (P_i) increased from 0.41 mm/yr in Mg-0.5Zn to 1.03 mm/yr in Mg-3Zn. As the amount of Zn increased, I_{corr} and P_i increased at around 2.5 fold, in other words, the corrosion resistant decreases as the Zn ratio increases. Corrosion rate of the as-cast Mg-Zn alloys following: Mg-3Zn > Mg-2Zn > Mg-1Zn > Mg-0.5Zn. The secondary phases such as MgZn act as a micro-cathodic sites which induced to the localized corrosion in Mg-3Zn alloy [10]. However, Mg-3Zn alloy which contained high relatively high volume fraction of secondary phase particles shows improvement in the general and localized corrosion resistance [16,17]. As corrosion resistance increased with the addition of Zn in SBF solution under as-cast conditions [16,17], the corrosion resistance decreased in this study. This difference may be due to the solution used in that studies. On the other hand, there are both as low as 0.8% NaCl in SBF and different chemicals (such as MgCl_2 , KCl, CaCl_2). Therefore, it is also necessary to consider the tendency of these chemicals to form a barrier on the surface during corrosion.

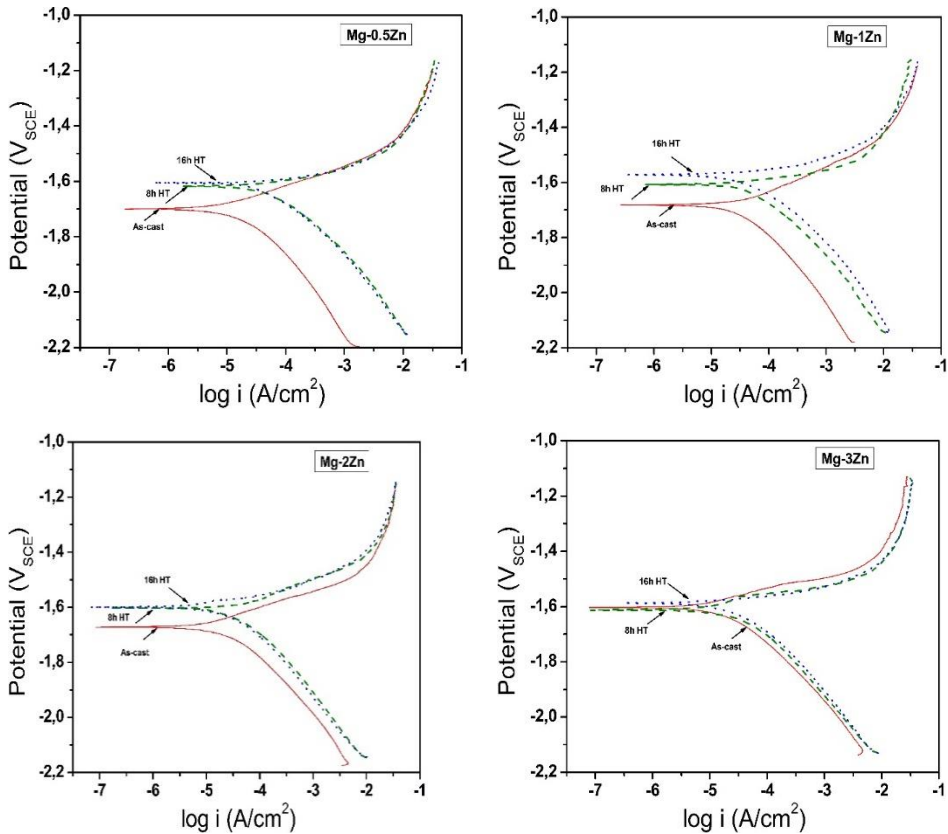


Fig. 4. Potentiodynamic polarization curves of the as cast and heat treated Mg-Zn alloys

In Fig. 4, polarization curves showed that as the amount of Zn increases, I_{corr} values decreased from 58 $\mu\text{A}/\text{cm}^2$ in Mg-0.5Zn to 28 $\mu\text{A}/\text{cm}^2$ in Mg-3Zn after 8 hours heat treatment and decreased from 45 $\mu\text{A}/\text{cm}^2$ in Mg-0.5Zn to 29 $\mu\text{A}/\text{cm}^2$ in Mg-3Zn after 16 hours heat treatment. Corrosion rate decreased from 1.33 mm/yr in Mg-0.5Zn to 0.64 mm/yr in Mg-3Zn after 8 hours heat treatment and decreased from 1.03 mm/yr in Mg-0.5Zn to 0.66 mm/yr in Mg-3Zn after 16 hours heat treatment. As the amount of Zn increased, I_{corr} and P_i values decreased by 50% and 35% after 8 hours and 16 hours of heat treatment respectively.

It can also be suggested that in the galvanic couple of Mg-3Zn, α -Mg matrix phase behaves as an anode and MgZn intermetallic phase behaves as a cathode. Therefore, after heat treatment (8 hours and 16 hours) corrosion rate of the as-cast Mg-Zn alloys following: Mg-0.5Zn > Mg-1Zn > Mg-2Zn > Mg-3Zn.

Table 2. Electrochemical data obtained from potentiodynamic polarization curves of as cast and heat treated Mg-Zn alloys.

Alloys		E_{corr} ($V_{Ag/AgCl}$)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	P_i (mm/yr)
As-cast	Mg-0.5Zn	- 1.70	18	0.41
	Mg-1.0Zn	- 1.68	33	0.76
	Mg-2.0Zn	- 1.672	40	0.93
	Mg-3.0Zn	- 1.653	45	1.03
8 hours heat treated	Mg-0.5Zn	- 1.617	58	1.33
	Mg-1.0Zn	- 1.607	56	1.29
	Mg-2.0Zn	- 1.602	39	0.91
	Mg-3.0Zn	- 1.612	28	0.64
16 hours heat treated	Mg-0.5Zn	- 1.604	45	1.03
	Mg-1.0Zn	- 1.572	38	0.88
	Mg-2.0Zn	- 1.60	32	0.75
	Mg-3.0Zn	- 1.586	29	0.66

4. Conclusions

- Microstructure studies showed that the grain size decreased with the increase of Zn content and the MgZn intermetallic phase was formed by the addition of 3 wt. % Zn. The grain boundaries are larger before heat treatment and grain structures are finer after heat treatment.
- Hardness test results showed that an increase of hardness by 36% was observed with increase of Zn content for the as-cast samples. The improvement of the hardness with the increasing of zinc additions can be explained by the grain refinement. Due to the solidification conditions for the as-cast samples, internal stresses are likely to be inevitable and this may also have caused the hardness to increase. The increase in hardness value of the samples subjected to 8 hours of heat treatment was 39%, while the values of 16 hours of heat treated samples increased to 58%. After heat treatment, it is expected that the internal stresses cause relaxation and the hardness of the heat treated samples decreased.

- For the as-cast samples, as the amount of Zn increased, I_{corr} and P_i increased at around 5.7 fold, in other words, the corrosion resistant decreases as the Zn ratio increases.
- As the amount of Zn increased, I_{corr} and P_i values decreased by 50% and 35% after 8 hours and 16 hours of heat treatment respectively. In other words, the corrosion resistant increases as the Zn ratio increases both after 8 hours heat treated and 16 hours heat treated samples. It can be suggested that in the galvanic couple of Mg-3Zn, α -Mg matrix phase behaves as an anode and MgZn intermetallic phase behaves as a cathode.

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