Microstructure Modification by Electron Beam Processing in Magnesium Alloys to Control the Degradation Rate

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Abstract

Electron beam processing (EBP) was applied on two different cast magnesium alloys (AZ91 and ZKX50) followed by subsequent heat treatment (HT). The microstructure and corrosion properties of the alloys in all of the conditions were investigated by standard microscopy and electrochemical measurements. After EBP, a uniform and significantly refined microstructure compared to the as-cast condition is observed. The grain size decreased notably and a more homogeneous distribution of the intermetallic phases is achieved. Electrochemical tests indicated that the AZ91 alloy exhibits higher corrosion resistance in EBP condition compared to EBP-HT and as-cast conditions after 1-day immersion in 3.5wt% NaCl solution. While the ZKX50 alloy shows higher corrosion resistance in EBP-HT compared to as-cast and EBP states after 1-day immersion in 0.5wt% NaCl solution. The corrosion behavior of magnesium alloys can be attributed to the grain size and distribution of the secondary phases. A connected Mg₁₇Al₁₂ network surrounding α-Mg grains in EBP AZ91 provides a barrier for the corrosion propagation from α -Mg grain to the neighbor grains and thus increases the corrosion resistance. Heat treatments at high temperature affect the corrosion resistance due to the dissolution of the β -phase network. In the case of ZKX50 alloy, the dissolution of Ca₂Mg₆Zn₃ secondary phases after heat treatment seems to provide higher corrosion resistance, while distributed secondary phases affect negatively the corrosion resistance of EBP ZKX50 compared to the as-cast condition due to the microgalvanic corrosion caused by these phases.

Keywords

Magnesium alloys; electron beam processing; microstructure modification; secondary phases

Introduction

Magnesium alloys owing their unique properties such as low density and high specific strength are used in a wide range of applications including automotive and aerospace applications. Moreover, magnesium alloys are attractive materials for use as biodegradable implants due to their great biocompatibility and mechanical properties similar to those of human bones [1]. However, their applications are limited due to their rapid corrosion rate. In general, the corrosion behavior of Mg alloys is significantly influenced by the microstructure, such as grain size, the size, and morphology of intermetallic compounds and their distribution, chemical segregation, as well as the presence of precipitates or impurities[2]. In the last decades, a wide range of research has been carried out to improve the corrosion resistance based on different approaches including the use of protective coatings[3],[4], developing new alloys and surface modification [5]. Microstructure modification by controlling the grain size, the volume fraction, size and distribution of the secondary phases is one of the strategies to control the corrosion of the magnesium alloys. Hence, the microstructure has a significant effect on the corrosion behavior of magnesium alloys, a refined microstructure obtained from a rapid solidification process can improve the corrosion properties [6],[7]. Supersaturation achieved using the rapid solidification technique leads to an increase in the matrix corrosion potential by addition of a more noble element in solid solution, which can be deleterious in the case of precipitation, since they can act as microgalvanic cells with respect to the matrix; and enhanced stability of the oxide layer through an increase in appropriate alloying additions. Moreover, the better homogeneity obtained using this technique through the microstructural element lowers the negative effect of impurities, such as sensitivity to pitting corrosion [8]. Different techniques are used for rapid solidification such as laser surface melting, centrifugal atomization, splat quenching, electron beam melting [8], [9], [10]. The improvements of wear and corrosion resistance of magnesium alloys after laser melting have been reported in several investigations [11], [12], [13]. Abbas et al. studied the effect of laser melting on corrosion resistance of Mg alloys AZ31, AZ61 and WE43, and their results indicate that the significantly improved corrosion resistance after treatment is a result of grain refinement and uniform redistribution of the intermetallic phases [12]. In addition to laser surface melting technique, electron beam processing (EBP) has been developed as a new high-power energetic beam used for surface modification of materials. It exhibits essential advantages over laser and ion beams by its high efficiency, simplicity, and reliability [14]. Recently, Liu et al. found that high current pulsed electron beam (HCPEB) treated Mg-4Sm shows the best corrosion resistance, which can be mainly attributed to the homogenous microstructure and composition after repeated melting and rapid solidification [15]. The present work aims to investigate the influence of electron beam processing on the microstructure modification of two magnesium alloys and the effect of the process and subsequent heat treatment on corrosion behavior of the alloys.

Materials and Methods

The materials used in this work were as-cast AZ91 magnesium alloy (Mg - 8.5 wt% Al - 0.76 wt% Zn - 0.21 wt% Mn) and a ZKX50 magnesium alloy (Mg- 5.2%Zn-0.2%Zr-0.13%Ca-0.09%Mn), similar to the alloy developed by [16]. The 9mm AZ91 and 6mm thick ZKX50 plates were cleaned with ethanol to remove any contamination on the surface. EBP was conducted on the surface of the plates using a Probeam EBG 45-150 K14 electron beam welding machine with its maximum accelerating voltage of 150kV, frequency of 300Hz and the focus position at the surface, in a 5×10^{-7} Torr vacuum chamber. The used parameters of the EBP for the alloys are listed in Table 1.

Table	1: Optimum	electron	beam	parameters	used for	microstructure	modification	of AZ91
				and Z	KX50			

Allow	Accelerating voltage U	Beam Current I _B	Beam Speed	Beam diameter
Alloy	(kV)	(mA)	v (mm/s)	Ø (mm)
AZ91	150	10	10	5
ZKX50	150	8	8	5

Subsequent heat treatment was applied to both EBP alloys: A solution heat treatment at 413°C for 16 hours followed by quenching according to ASTM B661-12 standard[17] in water was performed on AZ91 and solution heat treatment at the temperature of 330°C for 24 hours with subsequent water quenching for ZKX50 alloy. For the microstructural investigation, the specimens were sectioned transversely to the process direction, embedded in epoxy resin at room temperature to avoid any change of the microstructure. Thereafter, the samples were ground with SiC papers from P800 to P4000, polished by diamond paste up to 1µm and final step with colloidal silica (OPS) of 0.04µm. Scanning electron microscope (SEM), energy dispersive X-ray (EDX) and electron backscattered diffraction (EBSD) were used for microstructural investigation. The distribution of refined grains was determined by EBSD measurements. The corrosion resistance of the processed alloy and the as-cast condition was measured by electrochemical measurements, including open circuit potential (OCP), potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS). Experiments were carried out in a conventional corrosion cell, with a platinum foil as the counter, saturated Ag/AgCl as the reference. Since the higher concentration of aluminum has a beneficial effect on corrosion resistance of the magnesium alloys, the corrosion tests on AZ91 alloy was performed at 22 ± 0.5 °C in a 3.5% wt NaCl electrolyte, while 0.5% wt NaCl solution was used for ZKX50 alloy. Afterward, the results of the measurements were analysed using NOVA1.11 software. The surface of the samples for the corrosion test was ground up to P4000 SiC papers, cleaned with distilled water and air dried.

Results and discussion

Macroscopic view

Figure 1 exhibits the macroscopic view of the cross-section and the surface of the EBP AZ91 and ZKX50 alloys. The cross-sectional investigation of both EBP alloys (Figure 1 (a) and (c)) showed a complete penetration at the root with a depth of about 6mm and 5mm for AZ91 and ZKX50 alloys, respectively. The EBP was free of cracks or pores provoked by fast cooling rate during solidification. The processed surface of both alloys shows an acceptable appearance (Figure 1 (b) and (d)) for further experiments preparation.



Figure 1: Macroscopic pictures of (a, c) the cross-section and (b, d) the surface appearance of the EBP AZ91 and ZKX50 alloy. (BM is the base metal and EBP is the electron beam processed part)

Microstructure investigation

The microstructure of the alloys in the as-cast condition is shown in Figure 2. The results of the EDX measurements showed the as-cast AZ91 is composed of α -Mg, β -Mg₁₇Al₁₂ phase, (α + β) eutectic phase and a small amount of isolated Al-Mn particles. The as-cast ZKX50 alloy exhibited the Mg-Zn solid solution matrix and intermetallic phases (IMP). EDX analysis determined that lamellar phases are rich of Mg-Zn-Ca (Ca₂Mg₆Zn₃) along the grain boundaries and irregular shape particles contain Zn-Zr-Mn, distributed within the grains and on the grain boundaries. The intermetallic particles containing Zr rich are found to be the ones that are the major responsible for microgalvanic corrosion[18].



Figure 2: SEM micrographs of (a) as-cast AZ91 and (b) as-cast ZKX50 alloys

A significant grain refinement after the EBP was observed for both alloys as shown in Figure 3. Due to the rapid solidification during the EBP, the microstructure of both alloys is composed of fine equiaxial grains and the secondary phases were rearranged at the new grain boundaries of α -Mg. In the processed area, there was no evidence of micro defects such as cracks, pores, and segregation within the grains.



Figure 3: SEM micrographs of (a) EBP AZ91 and (b) EBP ZKX50 alloys

The inverse pole figure (IPF) maps obtained from the EBSD analysis are presented in Figure 4. This analysis showed fine and dendritic grains in the EBP AZ91 alloy and the nearly globular grains in EBP ZKX50 alloy is mainly due to the nucleation effect of Zr. The average grain size has been decreased from about 180 μ m to 15 μ m for AZ91 and from 70 μ m to 8 μ m for ZKX50 after EBP.



Figure 4: IPF maps of the EBP area for (a) AZ91 and (b) ZKX50 alloys

Figure 5 shows the heat treated microstructure of EBP AZ91 and ZKX50. The solution heat treatment of AZ91 causes to a total dissolution of the $(\alpha+\beta)$ eutectic. The very slow diffusion of aluminum in solid state α -Mg during solid solution treatment in AZ91 led to grain coarsening completely dissolution of the β phase into the α -Mg matrix. After water quench, the microstructure consists of supersaturated α -Mg and Al-Mn particles, as depicted in Figure 5a. Figure 5b shows the microstructure of EBP ZKX50 after homogenization treatment at 330°C for 24 hours. The EDX and SEM analyses reveal that the Mg-Zn-Ca secondary phases partially

dissolved in the α -Mg matrix without considerable grain coarsening due to the existence of Zn-Zr particles inhibiting the grain coarsening.



Figure 5: SEM micrographs of heat treated EBP (a) AZ91 and (b) ZKX50 alloys

Corrosion behavior

Open circuit potential (OCP) test

The open circuit potential (OCP) of the samples were carried out during 45 and 60 minutes for AZ91 and ZKX50 alloys, respectively. Figure 6 illustrates the OCP variations with the time for different microstructure conditions in both alloys.



Figure 6: Open circuit potential in as-cast and EBP and EBP-HT condition (a) AZ91 during 45minutes immersion in 3.5 wt% NaCl and (b) ZKX50 during 60minutes in 0.5wt% NaCl

As it can be seen in Figure 6 (a), AZ91 alloy in EBP condition had a higher OCP than as-cast and heat treated EBP conditions after 45 minutes immersing in 3.5wt% NaCl. The OCP of ascast AZ91 alloy showed an increase within the initial 5 minutes of immersing toward the positive direction from -1.625V to -1.610V which can be related to the formation of the magnesium hydroxide film or corrosion products on the surface [2]. Afterward, the potential slightly increased and for the last 20 minutes was stabilized at around -1.575V. This behavior is attributed to the stable growth of the corrosion layer [2]. EBP AZ91 showed a significant continuous increase of potential during the first 25 minutes from -1.635V to -1.520V. With increasing the time, the potential dropped to the more negative value (-1.535V) and stabilized at about -1.560V for the last 10 minutes of immersing. The higher fluctuation, in this case, indicates that the formation of the corrosion layer on the surface of the material for the EBP AZ91 alloy is more irregular compared to the other conditions. In heat-treated EBP AZ91, the OCP sharply increased from -1.650V to -1.605 immediately after immersing into the solution. Then it decreased gradually after about 13 minutes and it was stabilized at -1.645V for the last 25 minutes. As observed in Figure 6 (b), as-cast ZKX50 showed a slight decrease of OCP in the first moments of immersion then it increased slightly and stabilized at around -1.550V. EBP ZKX50 showed a lower OCP than as-cast at the beginning but the OCP increased by passing time until reaching to -1.400V and suddenly dropped and stabilized at -1.500V. Heat treated EBP ZKX50 showed a sinusoidal behavior at the beginning attributed to the formation and dissolution of protective surface film and stabilized at -1.500V. The increasing OCP after immersion is due to the growth of the corrosion layer, whereas a dynamic balance between the dissolution of magnesium and the deposit of corrosion product leads to a relatively stable OCP value [19].

Potentiodynamic polarization (PDP) test

The potentiodynamic polarization curves of the as-cast, EBP and EBP-HT alloys are shown in Figure 7. The corrosion current density i_{corr} and corrosion potential E_{corr} of both alloys in all three conditions obtained by applying Tafel extrapolation methods on potentiodynamic polarization curves are listed in Table 2. In general, an improvement of the corrosion resistance of the material is related to a reduction of the i_{corr} . As seen in Figure 7.a and according to table 2, i_{corr} of the AZ91 alloy after EBP is significantly reduced compared to the as-cast condition and it is higher in the heat treated state in comparison to the EBP condition. It suggests that the corrosion resistance of the EBP AZ91 is higher than the as-cast state. According to table 2 and as shown in Figure 7.b, i_{corr} of the EBP ZKX50 alloy is reduced after heat treatment in comparison to the EBP and as-cast conditions. Accordingly, the ZKX50 alloy suggests that the higher corrosion resistance in heat treated EBP condition.



Figure 7: Potentiodynamic polarization curves of as-cast and EBP and EBP-HT condition (a) AZ91 in 3.5 wt% NaCl and (b) ZKX50 in 0.5wt% NaCl

 Table 2: Electrochemical parameters in potentiodynamic polarization calculated by Tafel

 extrapolation

Alloy	Conditions	E _{corr} (V)	icorr (A/cm ²)	
	As-cast	-1.460	$39.03 imes10^{-6}$	
AZ91	EBP	-1.435	4.38 ×10 ⁻⁶	
	EBP-HT4	-1.426	15.10×10 ⁻⁶	
	As-cast	-1.471	37.46×10 ⁻⁶	
ZKX50	EBP	-1.410	50.05×10 ⁻⁶	
	EBP-HT	-1.453	26.48×10-6	

Electrochemical Impedance Spectroscopy (EIS) test

EIS measurements in the form of Nyquist plot were carried out after 1hour and 1day of exposure to 3.5wt% NaCl for AZ91 and 0.5wt% NaCl for ZKX50 alloys. Figure 8 and Figure 9 show the Nyquist plots for all three conditions. The radius of the capacitive loop for as-cast AZ91 after 1 hour was larger than the other conditions (~400 Ω .cm²). After the increase of immersion time to 1 day, the radius of capacitive loop increased significantly for EBP samples from ~250 Ω .cm² to ~500 Ω .cm², while it decreased for as-cast and heat-treated EBP samples (Figure 8.b). The radius of the capacitive loop for heat treated EBP ZKX50 samples is larger than in the other conditions for both immersion time. However, the radius of the capacitive loop decreased by increasing the immersion time for all three conditions. The capacitive loop in the as-cast state shows a more pronounced reduction compared to the others and is the smallest one after a 1day immersion (Figure 9). It is reported that the high-frequency part in the Nyquist plot represents the properties of the coatings, whereas the low-frequency part is associated with the Faradaic processes occurring on the bare metal [14, 15]. In case of Mg and their alloys, the presence of a thick oxide film itself behaves as a coating that protects the metal up to a certain level. Therefore, the observation of a capacitive behavior from the higher to the middlefrequency region is associated with the resistance of the corrosion layer. The capacitive loop is larger for the EBP AZ91 alloy, thus higher corrosion resistance of the corrosion products is observed for this condition. The higher impedance of the corrosion layer of the EBP AZ91is attributed to the barrier effect of the β -phase while with dissolving this phase after heat treatment the impedance decreased. As well as in the case of ZKX50, a better capacitive behavior of the EBP-HT sample can be attributed to the dissolution of the intermetallic phases that can act as microgalvanic cells.



Figure 8: Nyquist diagrams in as-cast, EBP and EBP-HT condition of AZ91 after (a) 1 hour and (b) 1-day immersion in 3.5 wt% NaCl



Figure 9: Nyquist diagrams in as-cast, EBP and EBP-HT condition of ZKX50 after (a) 1 hour and (b) 1-day immersion in 0.5 wt% NaCl

The electrochemical behavior of the EIS measurements was evaluated using a Randles equivalent circuit, as shown in Figure 10. The charge transfer resistance (R_{ct}), solution resistance (R_s), and double layer constant phase element (CPE_{dl}). A constant phase element was used instead of capacitance to account for the non-ideal behavior of the system [20] obtained from the Randles equivalent circuit for ZKX50 alloys. R_{ct} is related to the resistance for passage of ions through the corrosion layer, thus an indirectly related to the corrosion resistance, CPE_{dl} is related to the capacitance of the double layer on the electrolyte/metal interface; Rs is an uncompensated solution resistance. The inductive response observed at low frequencies is mainly related to the instability of the system and for simplification, it was not considered in the present work.



Figure 10: Example of measured and calculated Nyquist diagrams using the Randles equivalent circuit for an EIS measurement

From Table 3, it can be noted that R_{ct} of ZKX50 in all three conditions decreases with time, suggesting a decrement in their corrosion resistance. In opposite to R_{ct} , an increase of the CPE_{dl} values was measured for all three alloys from 1 h immersion to 1-day immersion, Table 3. CPE_{dl} is associated with the water/electrolytes uptake through the pores/defects of the surface film [17, 18], and the pores can generate pockets that act as a second capacitive loop. Normally unconnected small pores act as storage of ions, increasing the capacitance. On the other hand, with considering the same corrosion layer thickness it is easier for ions to go through the higher the porosity, thus decreasing the capacitance. Therefore, from 1 h to 1 day the thickness of the corrosion layer could increase, thus an increase CPE_{dl} with time implies the increase of porosities/defects in the oxide film. Increase of porosities in the film increases the diffusion reaction. The EIS measurements show similar behavior compared to the other electrochemical measurements. The EBP-HT shows higher corrosion resistance behavior among the tested conditions

Table 3: Simulated parameters of the electrochemical impedance spectroscopy (EIS) data ofthe investigated ZKX50 alloys after 1 and 24 h.

Alloy	Condition	Time (h)	$\operatorname{Rs}(\Omega)$	Rct (Ω cm2)	CPEdl (µF cm-2)
		1	37.73	698.00	44.20
	as-cast	24	35.14	365.29	85.30
722250	EDD	1	32.02	995.32	42.00
ZKA50	EBP	24	31.15	221.76	123.63
-		1	33.97	1742.50	41.40
	EBP-HI	24	33.25	741.11	87.59

Conclusion

The electron beam processing on the surface of AZ91 and ZKX50 magnesium alloys leads to a significant microstructure refinement with a homogenous distribution of the secondary phases at the grain boundaries. Both alloys do not show visible microsegregation due to the small grain size and higher cooling rate reached during the process. The results of electrochemical corrosion tests showed that these microstructural changes led to the improvement in corrosion resistance of the AZ91 alloy after EB processing. Solution heat treatment of the EBP AZ91 alloy decreases the corrosion resistance of the alloy due to the dissolution of the β -phase that can act as a barrier to the corrosion propagation. In the case of the ZKX50 alloy, there is no barrier effect. Thus, the smaller fraction of the intermetallic phases means higher corrosion resistance. Therefore the EBP-HT state shows the highest corrosion resistance among the other conditions.

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