J Mater Sci (2009) 44:4279–4285
DOI 10.1007/s10853-009-3634-1

The effect of skin characteristics on the environmental behavior of die cast AZ91 magnesium alloy

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Received: 29 March 2009 / Accepted: 20 May 2009 / Published online: 5 June 2009

Abstract The skin characteristics of die cast AZ91 magnesium alloys and their consequent environmental behavior were evaluated in correlation with die cast wall thickness. The metallurgical examination of the skins was carried out using scanning electron microscopy (SEM), SPX-surface analyses with ESCALAB 250 apparatus, and X-ray diffraction analysis. The corrosion behavior of the skins was evaluated by immersion tests and by potentiodynamic polarization measurements in 3.5% NaCl solution saturated with Mg $(OH)_2$ at room temperature. The results show that the corrosion resistance of die cast specimens with relatively greater thickness was improved compared to the corrosion resistance of thin wall specimens. This was explained in light of the obtained skin characteristics, mainly in terms of aluminum content, β phase ($Mg_{17}Al_{12}$) quantity and morphology, and level of porosity.

Introduction

The attractiveness of magnesium alloys as a dominant structural material for the transportation industry is inherently related to weight-saving concerns. However, one of the major disadvantages of magnesium alloys produced by high pressure die casting (HPDC) technology is their reduced corrosion resistance. Consequently, efforts were made to improve the corrosion resistance of these alloys, including optimization of the die casting process parameters.

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One of the interesting features of HPDC relates to the external skin of die cast components that apparently may have an important effect on the corrosion resistance. According to Shan and Gokhale [1], HPDC process of magnesium alloys invariably leads to a "skin effect", where the microstructure of the casting near the free surfaces differs significantly from that in the interior. They indicated that the skin region has much finer microstructure and smaller dendrite cell size, and that the amount of microporosity in that region also differs from that in the interior.

Song et al. [2] reported that the skin of die cast AZ91 D showed better corrosion resistance than the interior. They explained their findings by attributing the beneficial effect of the skin to the volume fracture and distribution of β phase in the vicinity of α grains. However, an opposite conclusion was obtained by Yu and Uan [3]. Their study on the correlation between the microstructure of die-chill skin and corrosion properties of AZ91 D obtained by HPDC indicated that samples without the die skin on the surface corroded more slowly. The inferior corrosion performance of the die skin was considered to be related to the high volume fraction of the interdendritic network of Al-rich α phase contained in the die skin, owing to the high cooling rate during solidification. The results of Yu et al. were also supported by Lafront et al. [4], who evaluated the corrosion resistance of die cast AZ91 D alloy in 0.05 M NaCl solution using electrochemical noise technique and electrochemical impedance spectroscopy. Lafront et al. found that at a depth between 10 and 50 μm, identified as the skin, all specimens showed general non-uniform corrosion with the lowest corrosion resistance compared to the interior section. In addition, they have indicated that frequently the exterior skin in the form of spherical skin tends to disappear during preparation of the specimen for examination.

Relating to the complex effect of β phase, Ghali et al. [5] indicated that the β phase serves a dual purpose in corrosion. The β phase can act either as a barrier for corrosion attack or as a galvanic cathode that can accelerate the corrosion degradation. According to Song et al. [6], the volume fraction of β phase can have a vital effect on the corrosion process of the α matrix. If the volume fraction of β phase is relatively high, the β phase may improve overall corrosion resistance. According to Zhao et al. [7], the β phase in AZ91 can act as a corrosion barrier and hinder corrosion propagation in the matrix if this phase is in the form of a continuous network. In relation to the surface film (i.e., skin), they indicated that this film can be more or less effective in hindering corrosion and more or less effective in controlling the form of corrosion as uniform corrosion or localized corrosion. The observations of Zhao et al. were supported by the findings of Uan et al. [8], who found that if the primary β phase on the die skin of AZ91 D is irregularly shaped and does not have a network structure, the removal of this phase did not improve the corrosion performance of the skin.

Another important parameter that has to be addressed relates to the solidification conditions of magnesium alloys during the HPDC process. According to Weiler et al. [9], regions of different solidification conditions show different measured skin thickness. The solidification conditions can also affect the chemical composition of the alloy in the skin layer. According to Cho et al. [10], the chemical composition at the surface of die cast AZ91 D alloy can have greater concentration of alloying elements composing the alloy. The redistribution of alloying elements and impurities during the solidification process and the preferred enrichment of alloying elements and impurities at the skin can inherently modify the corrosion resistance of the skin. In relation to the solidification rate, Song and Atrens [11] indicated that a faster solidification rate can improve the corrosion performance of the skin. This is obtained by increasing the ratio of β phase barriers, making α grains finer, making the β phase more dispersed and continuous, and reducing the amount of porosity. They even suggested that the original surface of a die casting should not be machined, as machining would remove the casting skin, which is much more protective than the casting interior.

The present investigation was initiated in light of the controversial views in the literature relating to the effect of skin characteristics on the corrosion performance of die cast magnesium alloys in general and AZ91 D alloy in particular. This was especially related to the correlation between die cast wall thickness and the formation of related skins that consequently affect the corrosion performance. Hence, the aim of this study is to evaluate the skin characteristics of AZ91 D magnesium alloy in correlation with die cast wall thickness. The obtained characteristics will be also correlated to the environmental behavior of the skin.

Experimental procedure

The chemical composition of AZ91 D magnesium alloy used in this investigation was in accord with ASTM B94/B94M standard and has the following composition (in wt%): 8.49% Al, 0.65% Zn, 0.17% Mn, 0.013% Si, 0.0005% Cu, 0.0010% Ni, 0.0008% Fe, with magnesium as the balance. The variations in skin characteristics were obtained by die casting rectangular specimens (200 mm length $\times$ 12 mm width) with different thicknesses: 1.5, 3, 6, and 9 mm, which represent actual dimensions of common die cast applications. Specimens with various thicknesses were cast in the same die using an IDRA OL-320 cold chamber die casting machine. The melt and die temperatures were 650–670 °C and 150–180 °C, respectively.

The microstructure analysis was obtained by scanning electron microscopy (SEM) with an energy dispersive spectrometer (JEOL JSM-5600). The SPX-surface analyses were performed using ESCALAB 250 apparatus that combines the Auger Electron Spectroscopy (AES) and the Scanning Auger Electron Mapping (SAM). The XPS analysis was also operated with Ar-Sputtering depth profile using the EX05 Ion Gun with Sputtering rate of 10 nm/min. The phase identification and relative amount was obtained by X-ray diffraction analysis using a Rigaku-2100 diffractometer with CuK_{α} wavelength. The X-ray tube parameters were 40 kV/30 mA and the scanning rate was 2°/min,

The corrosion performance of the different skins was evaluated by standard immersion tests including measurement of hydrogen evolution and by potentiodynamic polarization measurements. The polarization analysis was carried out using a Gamry PCI4/750 potentiostat with a scanning rate of 0.167 mV/s according to ASTM G5-94 standard. The corrosive environment for analysis, immersion, and polarization tests was 3.5% NaCl solution saturated with $Mg(OH)_2$. Both corrosion tests were carried out at room temperature.

Results and discussion

The typical microstructures of AZ91 D alloy at a transverse cross-section of rectangular die cast specimens with 1.5 mm and 6 mm thickness are shown in Fig. 1. This revealed that the grain size at the skin and away from the surface was significantly larger in the specimen with 6 mm thickness compared to the 1.5 mm specimen. In addition, it was clearly evident that the porosity level in the specimen

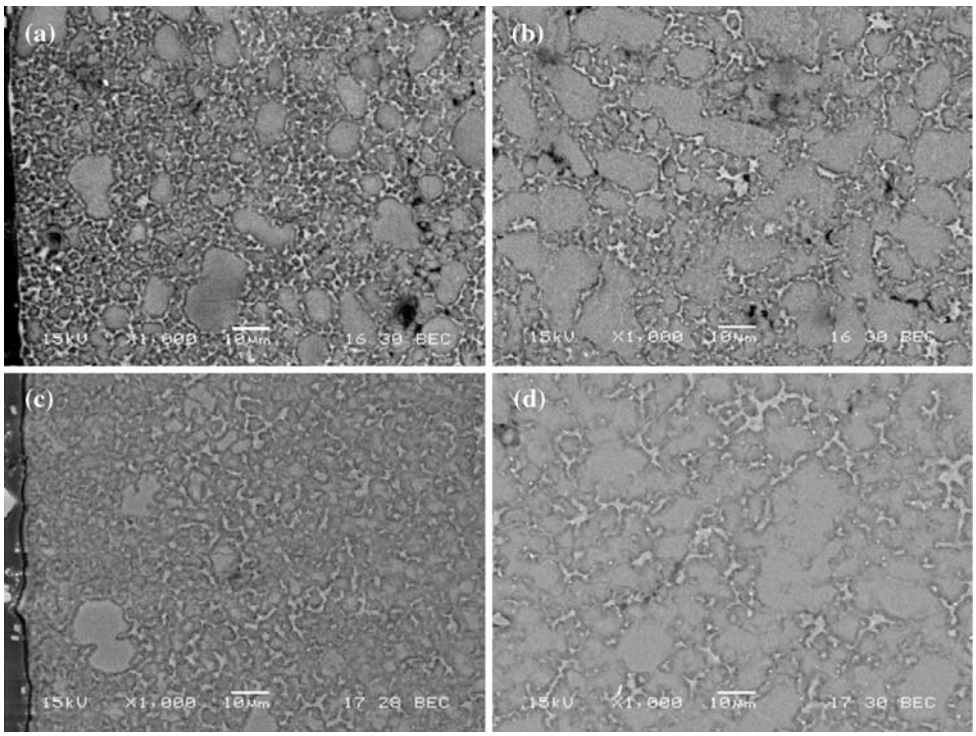

Fig. 1 Typical microstructure at transverse cross-section close to the external surface and at mid-section obtained by SEM microscopy. **a** and **b** Specimens with 1.5 mm thickness; **c** and **d** Specimens with 6 mm thickness. Images on the left are from the skin region and those on the right are from the interior

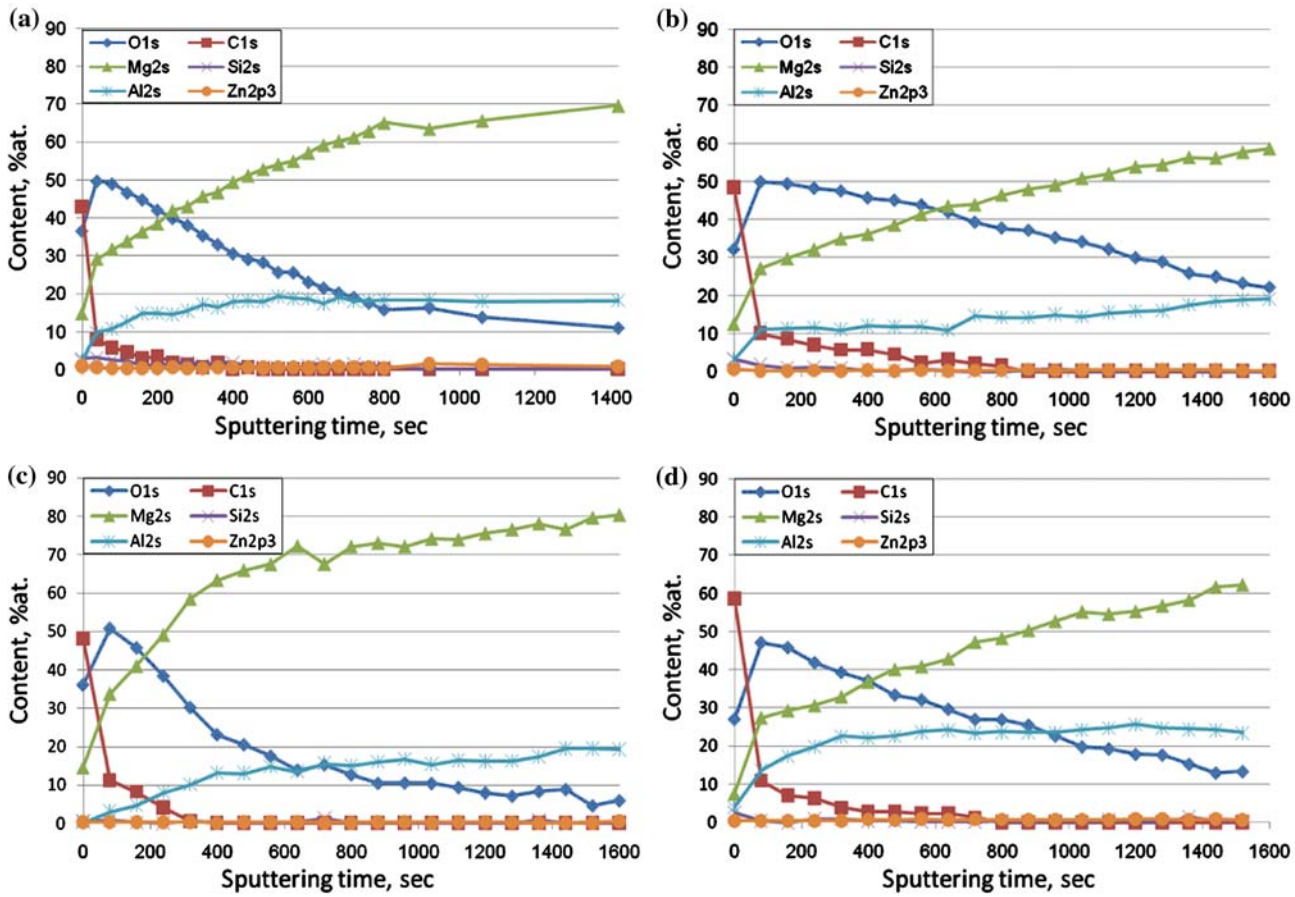

Fig. 2 Line profile of elements obtained by incorporating XPS analysis and Argon-sputtering at the surface of rectangular specimens with different thicknesses. **a** 1.5 mm, **b** 3 mm, **c** 6 mm, **d** 9 mm

with 1.5 mm thickness was significantly greater compared to the porosity content in the 6 mm specimen. The differences in grain size and porosity level versus wall thickness are related to the variations in the solidification conditions and to the high turbulent flow of molten metal in the thin wall specimens [12, 13].

The line profile of elements at the skin of rectangular specimens with 1.5, 3, 6, and 9 mm thickness as obtained by the SPX analysis (combined with Ar-sputtering) is shown in Fig. 2. This has mainly highlighted the fact that the aluminum content in the thick-walled specimen was greater than that of the thin-walled specimen as shown in Fig. 3. In addition, in order to identify the presence of impurities (e.g., iron and copper) that have a significant detrimental effect on the corrosion resistance of the tested alloy, the binding energy of the elements composing the skins of specimens with 1.5, 3, 6, and 9 mm thickness were evaluated by XPS analysis (incorporated with Ar-Sputtering) as shown in Fig. 4. This clearly indicated that the amount of impurity elements, iron (at 706.80 eV) and copper (at 932.67 eV), were extremely low and practically negligible.

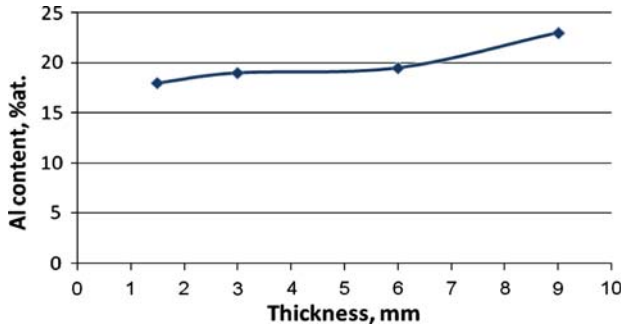

Fig. 3 Correlation between aluminum content at the skin and the thickness of the rectangular specimens as obtained by the XPS analysis

Typical X-ray diffraction analysis results obtained from the skins of specimens with 1.5, 3, 6, and 9 mm thickness are shown in Fig. 5. This revealed that the amount of β phase ($Mg_{17}Al_{12}$) in thick-walled specimens was greater than in the thin-walled specimens as highlighted in Fig. 6.

The corrosion resistance of rectangular specimens with 1.5, 3, 6, and 9 mm thickness in terms of immersion test in 3.5% NaCl solution saturated with $Mg(OH)_2$ is shown in Fig. 7. It should be pointed out that the corrosion rate was calculated from the amount of hydrogen evolved in the solution according to the following overall reaction:

$$2Mg + 2H^+ + 2H_2O \rightarrow 2Mg^{2+} + 2OH^- + 2H_2$$

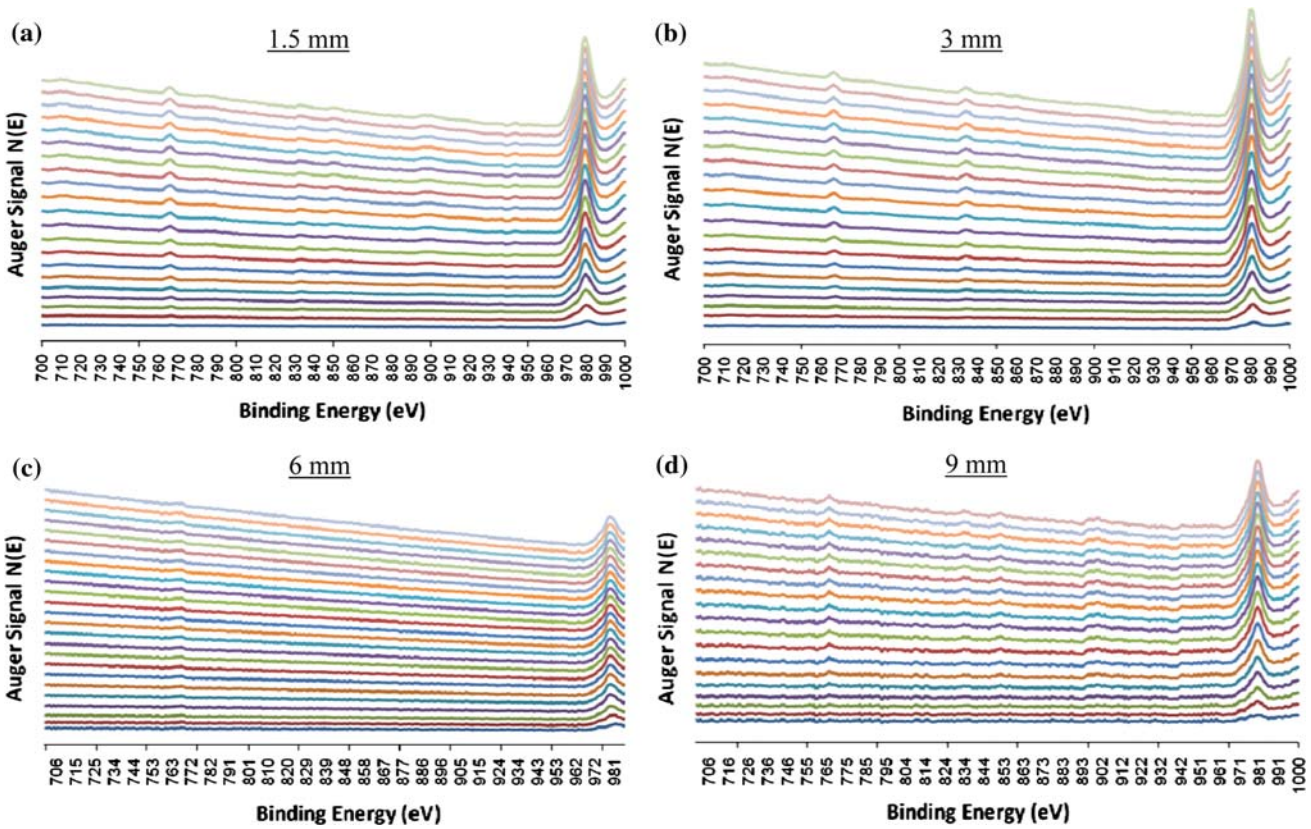

Fig. 4 XPS analysis (incorporated with Ar-Sputtering) at the skin of rectangular specimens with different thickness showing nearly no evidence of iron (706.80 eV) or copper (937.67 eV). **a** 1.5 mm, **b** 3 mm, **c** 6 mm, **d** 9 mm

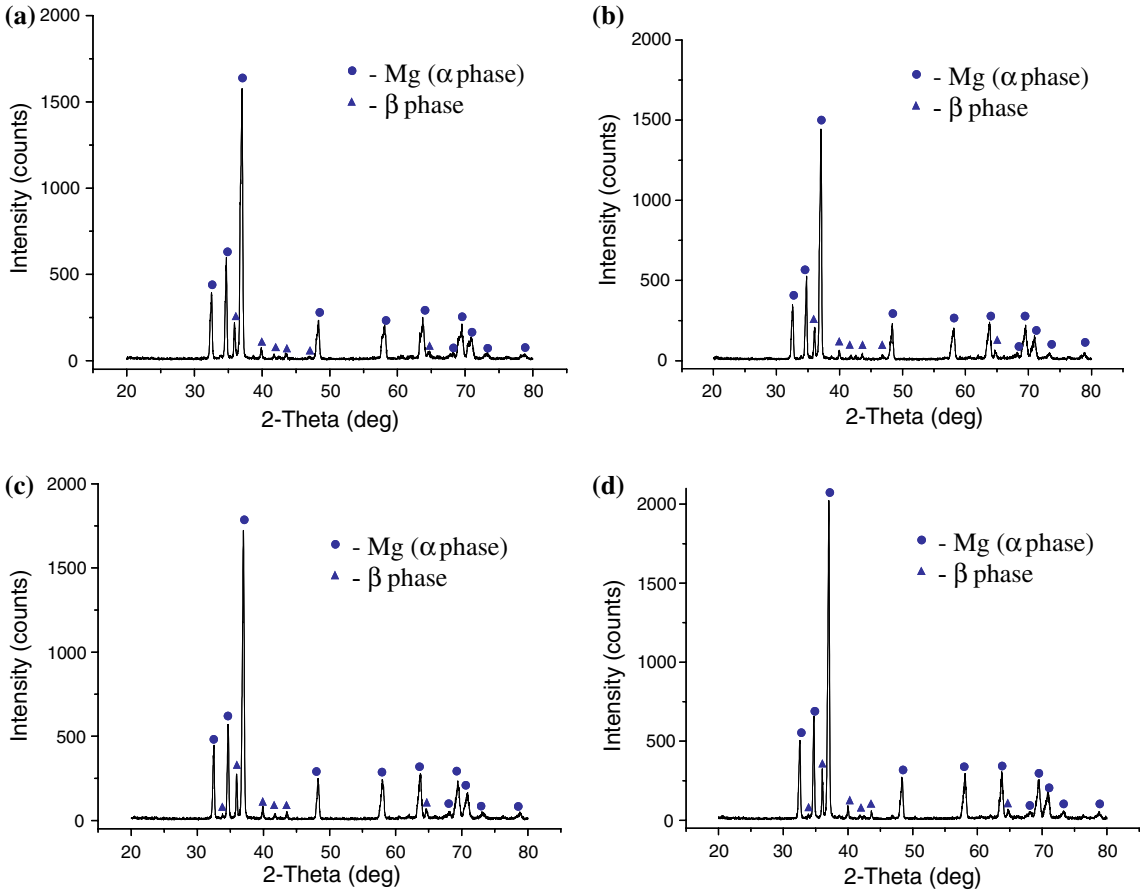

Fig. 5 X-ray diffraction analysis obtained from the skin surface of rectangular specimens with different thickness. **a** 1.5 mm, **b** 3 mm, **c** 6 mm, **d** 9 mm

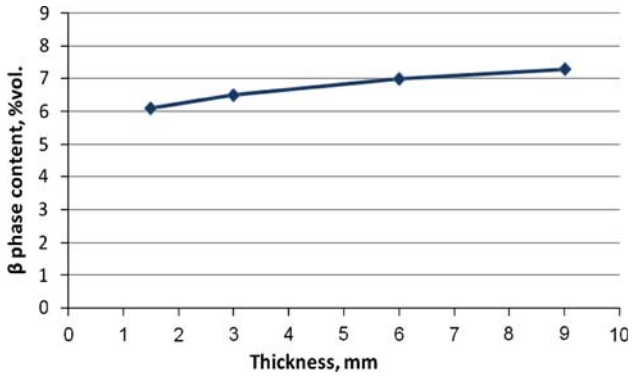

Fig. 6 Volume fraction of β phase at the skin versus thickness of the rectangular specimens

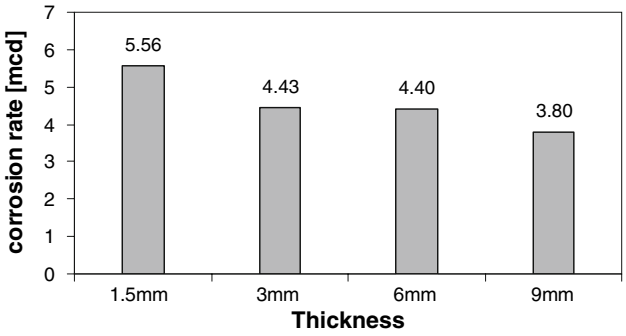

Fig. 7 Corrosion rates obtained from immersion tests of rectangular specimens with different thickness after 72 h exposure in 3.5% NaCl solution saturated with $Mg(OH)_2$

According to this hydrogen-evolution method, [14] the dissolution of one mole of magnesium corresponds to the evolution of one mole of hydrogen gas; hence the weight loss of magnesium in solution can be evaluated by the amount of hydrogen gas released during the corrosion process. The results obtained have clearly shown that the corrosion rate was reduced as the rectangular specimen became thicker. This result was also supported by the potentiodynamic polarization analysis carried out in the same corrosive solution as shown in Figs. 8 and 9.

Based on the obtained results for AZ91 D magnesium alloy, a summary of the skin characteristics and their corrosion resistance versus die cast specimen thickness is shown in Table 1. This is followed by a schematic

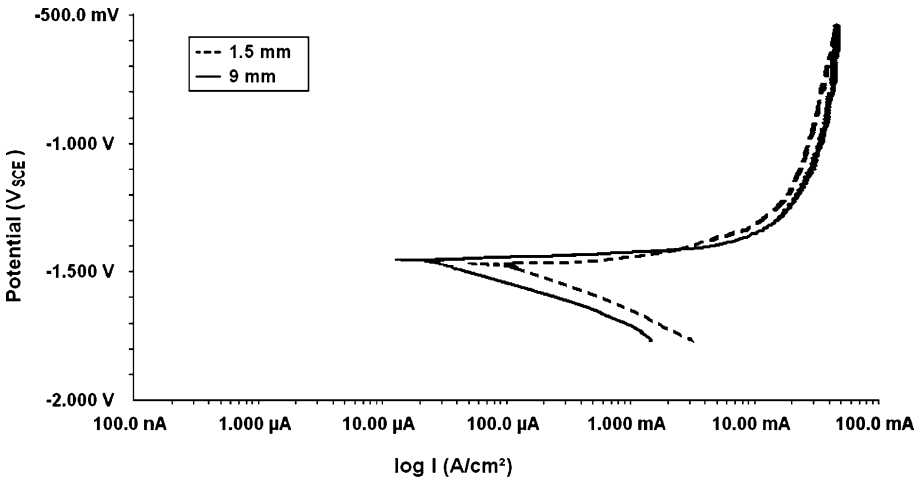

Fig. 8 Typical potentiodynamic polarization results obtained from rectangular specimens with 1.5 mm and 9 mm thickness in 3.5% NaCl solution saturated with $Mg(OH)_2$

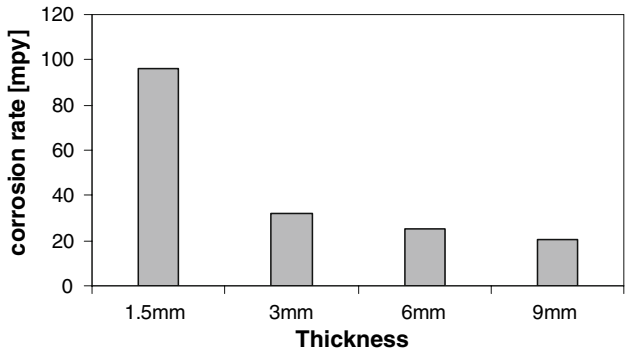

Fig. 9 Corrosion rates calculated from the potentiodynamic polarization analysis of rectangular specimens with different thickness after exposure to 3.5% NaCl solution saturated with $Mg(OH)_2$

Table 1 Skin characteristics and corrosion performance versus die cast specimen thickness for AZ91 D magnesium alloy

	Thin specimen	Thick specimen
Grain size	Small	Large
Aluminum content	Low	High
β phase content	Low	High
Porosity	High	Low
Corrosion resistance	Low	High
Heavy elements causing microgalvanic effect (e.g. Fe and Cu)	Negligible amount	Negligible amount

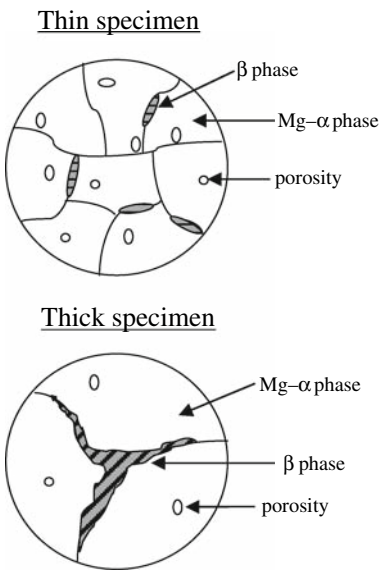

Fig. 10 Schematic illustration of skin characteristics versus die cast specimen thickness

illustration that highlights the differences between the skins of thin and thick specimens in terms of their microstructure network as shown in Fig. 10. According to the above summary and schematic illustration, the improved corrosion resistance of thick specimens compared to thin specimens is attributed mainly to the increased aluminum content and consequently the increased amount of β phase and the reduced level of porosity. Relating to the role of β phase in NaCl solution, Ghali et al. [5] and Song and Atrens [14] have already indicated that the β phase can have dual influences on corrosion—as a barrier and as a galvanic cathode—depending on the volume fraction of β phase in the α matrix. Song and Atrens also concluded that if the volume fraction of β phase was small, the β phase mainly served as a galvanic cathode and accelerated the corrosion process of the α matrix. Hence, according to the results of the present investigation it is believed that the limited amount of β phase in the skin of thin specimens causes the β phase to act as a galvanic cathode and consequently reduce the corrosion resistance of that skin. Contrarily in the case of thick specimens, the amount of β phase in the skin is large enough that the β phase can act as an anodic barrier that inhibits the corrosion process. In view of the microstructure network of β phase in the skin of thick

specimens (as shown by the schematic illustration), it is believed that in this case the β phase provides an adequate continuous network over the α phase and hence improves the overall corrosion resistance. This is again due to the relatively passive nature of β phase that was also found by Lunder et al. [15]. According to Lunder et al., the corrosion potentials of α Mg and β phase in 5% NaCl solution saturated with $Mg(OH)_2$ were -1.65 and -1.20 V_{SCE}, respectively, indicating comparatively improved corrosion resistance of β phase. Relating to the detrimental effect of heavy elements such as Fe and Cu on the corrosion resistance of the skins [16], this was eliminated in the present investigation by careful control of the chemical composition of the tested alloy and by an adequate die casting process.

Conclusion

The results obtained in the present investigation clearly demonstrate the correlation between the die cast wall thickness and the corrosion performance of the related skins. According to this correlation, the corrosion resistance of die cast AZ91 D magnesium alloy in 3.5% NaCl solution saturated with $Mg(OH)_2$ improved as the thickness of the die cast specimens was increased. The comparatively improved corrosion resistance of thick specimens was mainly attributed to the increased amount of Al and β phase in their skins and to the relatively reduced level of porosity.

Acknowledgements The authors would like to thank the Magnesium Research Institute of Dead Sea Magnesium for the preparation of the die casting specimens, and N. Frumin and D. Mogilyanski from Ben-Gurion University for their kind assistance in the XPS and XRD analyses, respectively.

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