

Original

Zander, D.; Heilig, M.; Hort, N.; Klaus, G.; Buehrig-Polaczek, A.; Groebner, J.; Schmid-Fetzer, R.:

Influence of cerium on the formation of micro-galvanic corrosion elements of AZ91

Materials Science Forum, Light Metals Technology V (2011)
Trans Tech Publications

DOI: [10.4028/www.scientific.net/MSF.690.381](https://doi.org/10.4028/www.scientific.net/MSF.690.381)

Influence of cerium on the formation of micro-galvanic corrosion elements of AZ91

Daniela Zander^{1, a}, Meredith Heilig¹, Norbert Hort², Gerald Klaus³,
Andreas Bührig-Polaczek³, Joachim Gröbner⁴ and Rainer Schmid-Fetzer⁴

¹Dept. of Biochemical and Chemical Engineering, TU Dortmund, D-44221 Dortmund, Germany

²HZG Research Centre, D-21502 Geesthacht, Germany,

³Foundry Institute of RWTH Aachen, D-52056 Aachen, Germany

⁴Institute of Metallurgy, TU Clausthal, D-38678 Clausthal-Zellerfeld, Germany

^adaniela.zander@bci.tu-dortmund.de

Keywords: AZ91D, cerium, corrosion, microstructure

Abstract.

Investigations of AZ91D revealed a strong influence of mainly the following microstructural parameters on corrosion: porosity, the eutectic, the Al-content of the Mg-phase as well as the volume fraction and distribution of gamma-Al₁₂Mg₁₇. Further an improved corrosion resistance was observed by the addition of rare earth elements. The influence of Ce on microstructure and corrosion of sand cast and high pressure die cast AZ91D with 0.5-2.0 wt.% Ce was investigated by SEM before and after potentiodynamic polarization measurements in pH7.5 (bi-distilled water adjusted with KOH). It was observed that Ce significantly improved the corrosion resistance by changing the microstructure. A strong influence of Ce on the average grain size, the fraction of the eutectic, changes in morphology and/or volume fraction of gamma Al₁₂Mg₁₇ and formation of a Ce-rich intermetallic phase was observed. Therefore, not only the chemical composition but also the change of microstructure and the formation of micro-galvanic elements influence the local corrosion mechanism of AZ91D with cerium.

Introduction

Magnesium-aluminum based alloys, such as AZ91D are one of the common alloy systems for the automotive industry. Unfortunately, magnesium has a number of undesirable properties including high chemical reactivity and poor resistance to degradation, such as corrosion. However, significant advances were reported in the development of corrosion resistant magnesium alloys during the last decades. It was observed that the reduction of impurities, the addition of alloying elements and heat treatments cause an improved corrosion behavior [1,2]. Further, the corrosion of magnesium alloys is known to depend strongly on the casting technique [3,4]. Differences in melt temperatures and solidification rates involved in each casting process lead to differences in the macrostructure, e.g. casting defects, porosity and microstructure, such as the formation of different phases and their distribution. It is well known that the corrosion behavior can be explained by the influence of the following major microstructural aspects: porosity, volume fraction and distribution of the gamma-phase (Mg₁₇Al₁₂) and aluminum content in the magnesium phase [5,6,7].

While the Mg(OH)₂ passive layer of magnesium is not stable below pH 11, it is assumed that additions of certain alloying elements assist stabilization of the passive layer [3,4,7]. Small additions of Ca, Y or Ce are acknowledged to improve the corrosion properties [8-12]. A recent study reports that Ce increases the protective nature of corrosion products through the assimilation of CeO₂ into the protective surface layers of Mg(OH)₂ [13]. When added to Mg-Al-Zn alloys, Ce has been reported to modify grain size and refine Mg₁₇Al₁₂ particle size [14]. However, the influence of Ce on the formation of a passive layer and on the corrosion resistivity limited by the microstructure, e.g. secondary phases, grain refinement are not clarified yet. This work investigates the influence of Ce additions on the microstructure and corrosion resistance of AZ91D.

Experimental

The influence of cerium on the microstructure and corrosion behavior of sand (Triplex) cast [15] AZ91D with 0.5 or 2.0 wt.% Ce and high pressure die cast AZ91D (HZG, Geesthacht, Germany / RWTH Aachen, Germany) was investigated. The sand cast alloys were prepared from the same pre-alloy AZ91D to control the influence of impurities on the corrosion measurements (Table 1).

Table 1: Composition of HPDC AZ91D and sand (Triplex) cast AZ91D with 0.5 or 2.0 wt.% Ce obtained by spark optical emission spectroscopy.

	Al [wt.%]	Zn [wt.%]	Mn [wt.%]	Si [wt.%]	Fe [wt.%]	Cu [wt.%]	Ni [wt.%]	Ce [wt.%]	Mg [wt.%]
HPDC AZ91D	8.11	0.736	0.224	0.015	<0.0006	0.003	<0.002	<0.004	bal.
Triplex AZ91D	8.98	0.852	0.270	0.017	<0.0006	0.002	<0.002	<0.019	bal.
Triplex AZ91D / 0.5Ce	8.97	0.764	0.289	0.011	<0.0006	0.002	<0.002	0.461	bal.
Triplex AZ91D / 2Ce	8.47	0.77	0.266	0.018	0.001	0.003	<0.002	1.89	bal.

For all corrosion measurements a three electrode electrochemical cell was used, with Ag/AgCl as a reference electrode and a platinum counter electrode. Potentiodynamic polarization curves were obtained using a FAS1 potentiostat (Gamry Instruments) with 0.5 mV/s at pH7.5. The pH of bi-distilled water was adjusted by KOH and kept constant at pH 7.5. Discussing the corrosion rate obtained from potentiodynamic measurements one has to take into account the strong cathodic hydrogen reaction as well as the different corrosion mechanism of magnesium alloys [16]. The samples were polished up to 1 μ m with a water free alcoholic solution in order to avoid deterioration by corrosion. The microstructure was investigated by X-ray diffraction, optical microscopy and SEM+EDS (Hitachi S-4500) before and after potentiodynamic measurements. Phase fraction was assessed by using the point-count method [17] with a 5x5 point grid. Average grain size was measured using the line-intercept method as described in the ASTM-E112 standard.

Results and Discussion

Microstructural investigations by optical microscopy of AZ91D revealed a much smaller average grain size for the high pressure die cast in comparison to the sand cast alloy (Fig. 1). This can be explained by the much faster cooling rate for the high pressure die cast alloy [18]. Further, the addition of up to 2 wt.% Ce leads to an increase of the average grain size for sand cast AZ91D.

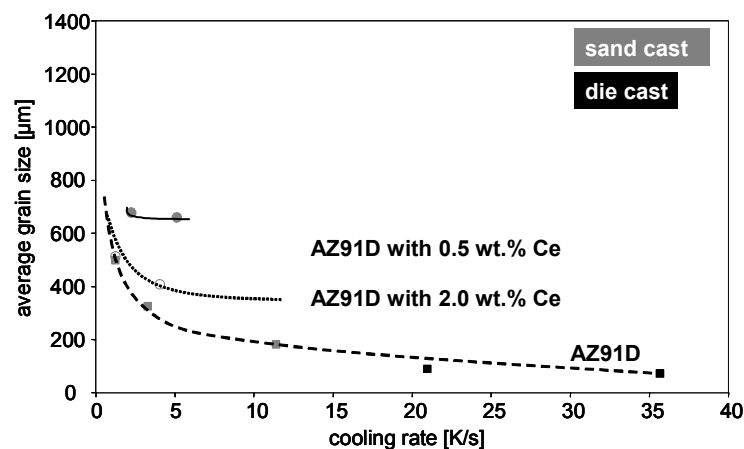


Figure 1: The effect of casting method and cerium additions on the average grain size of AZ91D.

Former investigations revealed the formation of Mg dendrites and eutectic, Al₁₂Mg₁₇ at the grain boundary phase and some porosity for all investigated alloys [18]. The high pressure die cast AZ91D exhibits a broad Mg grain size distribution and the formation of a discontinuous net of the Al₁₂Mg₁₇ grain boundary phase. In addition an increasing Al-concentration towards the Mg grain

boundary was observed [4,5]. Comparing the microstructure of high pressure die cast with sand cast AZ91D obtained with the highest cooling rate, a homogenous grain size distribution of coarse Mg dendrites, a similar $\text{Al}_{12}\text{Mg}_{17}$ phase fraction and a smaller fraction of the eutectic around or nearby the coarse $\text{Al}_{12}\text{Mg}_{17}$ phase were observed for the sand cast alloy. Figure 2 reveals that the addition of up to 2wt.% Ce results in the precipitation of finer $\gamma\text{-Al}_{12}\text{Mg}_{17}$ particles. In addition a larger rod-like Ce-rich phase and a few acicular Ce-rich precipitates are seen. X-ray diffraction indicated the formation of Al_2Ce and $\text{Al}_{11}\text{Ce}_3$ for 2wt.% Ce [18]. Further, an increase of the fraction of the overall Al-Ce phases and a decrease of the $\text{Al}_{12}\text{Mg}_{17}$ phase with increasing Ce-content was observed for sand cast AZ91D (Fig. 3a). The phase fraction of the eutectic was similar and independent from the Ce-content for the investigated sand cast alloys.

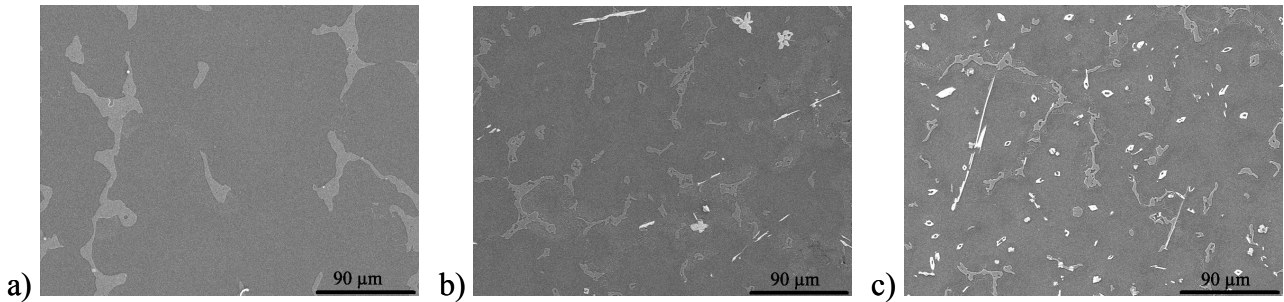


Figure 2: SEM images of the center of a) sand-cast AZ91D, b) sand cast AZ91D with 0.5wt.% Ce and c) sand cast AZ91D with 2wt.% Ce.

Potentiodynamic polarization measurements of high pressure die cast and sand cast AZ91D obtained with the highest cooling rate revealed similar corrosion rates in pH 7.5 (Fig. 3b). Whereas, a decrease of the corrosion rate with the addition of Ce was observed.

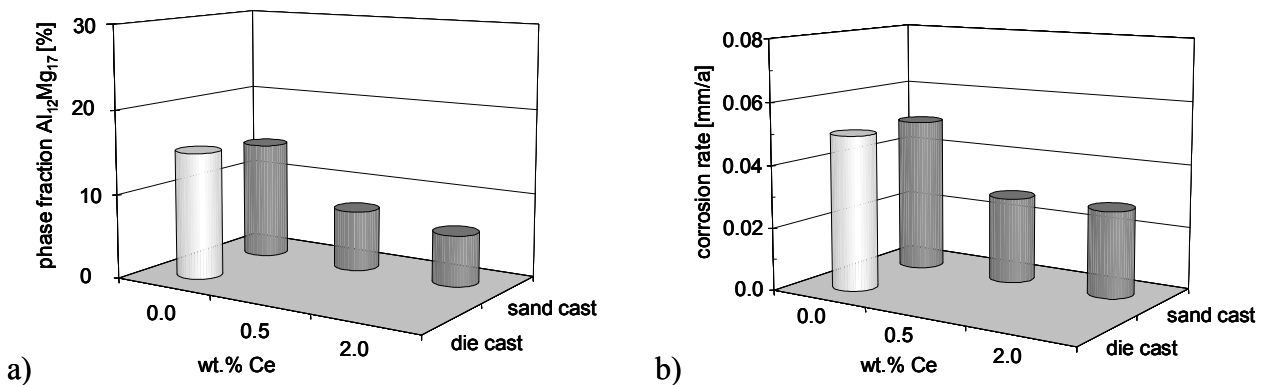


Figure 3: The influence of casting method and Ce-content on a) $\text{Al}_{12}\text{Mg}_{17}$ phase fraction and b) the corrosion rate.

Since the volume fraction and distribution of the $\text{Al}_{12}\text{Mg}_{17}$ phase and Al-content of the Mg-grains have a major influence on the formation of micro-galvanic elements in magnesium-aluminum alloys it is assumed that the addition of Ce leads to a decrease of the number of micro-galvanic elements by lowering the $\text{Al}_{12}\text{Mg}_{17}$ phase fraction in AZ91D (Fig. 3a).

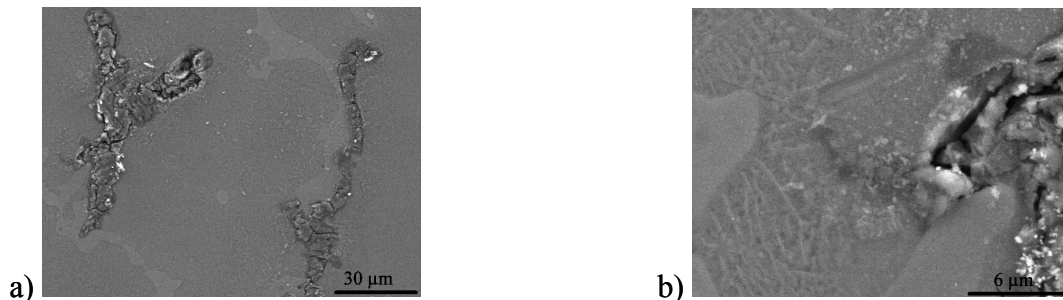


Figure 4: SEM images of sand cast AZ91D after potentiodynamic measurements in pH 7.5.

Figure 4 shows the corrosion damage after potentiodynamic measurements of sand cast AZ91D in pH 7.5. There is evidence that the nucleation of corrosion starts at the eutectic located around or nearby the coarse $Al_{12}Mg_{17}$ phase and not within the magnesium grain. However, since the eutectic itself also reflects a micro-galvanic element of $Al_{12}Mg_{17}$ and magnesium additional corrosion studies are underway to investigate the nucleation of the corrosion in regard to the microstructure of AZ91D alloys without and with Ce in more detail.

Conclusions

The present investigations revealed that the addition of Ce leads to a significantly improved corrosion resistance of AZ91D using common casting methods, such as sand casting. In addition a strong influence of Ce on the microstructure regarding higher average grain size with increasing Ce content and changes in the volume fraction of the $Al_{12}Mg_{17}$ phase in the bulk material was observed. This can be related to the formation of $Al_{11}Ce_3$ and Al_2Ce intermetallic phases. Further, the sand casting process revealed a similar corrosion rate in comparison to the high pressure die cast AZ91D in pH7.5.

Acknowledgment

The authors like to thank the Deutsche Forschungsgemeinschaft (German Research Foundation) for the financial support under the project Za 426/3-1.

References

- [1] J.D. Hanawalt, C.E. Nelsen, J.A. Peloubet: *Trans. AIME* Vol. 147(1942), p.273
- [2] O. Lunder, T. Kr. Aune, K. Nisancioglu: *Corrosion* Vol. 43 (1985), p. 247
- [3] S. Mathieu, C. Rapin, J. Hazan, P. Steinmetz: *Corrosion Sci.* Vol. 44 (2002), p. 2737
- [4] R. Ambat, N.N. Aung, W. Zhou: *Corrosion Sci.* Vol. 42 (2000), p. 1433
- [5] C. Pieper, *Fortschritt-Berichte VDI, Reihe 5, Nr. 711, VDI-Verlag, Düsseldorf* (2005).
- [6] D. Zander, C. Pieper, U. Köster, in: *Proc. of the 7th Int. Conf. Magnesium Alloys and Their Applications*, edited by K.U. Kainer, Wiley-VCH Verlag, Weinheim (2007), pp.757.
- [7] G. Song, A. Atrens, M. Dargusch: *Corrosion Science* Vol. 41 (1999), p. 249
- [8] A.A. Luo: *Mater. Sci. Forum* Vol. 57 (2003), p. 419.
- [9] E.D. Morales, E. Ghali, N. Hort, W. Dietzel, K.U. Kainer: *Mater. Sci. Forum* Vol. 867 (2003), p. 419
- [10] Y. Fan, G. Wu, H. Gao, C. Zhai: *Mat. Sc. Forum* Vol. 488-489 (2005), p. 869
- [11] N. Winzer, A. Atrens, G. Song, E. Ghali, W. Dietzel, K.U. Kainer, N. Hort, C. Blawert: *Adv. Eng. Mater.* Vol. 7 (2005), p. 659
- [12] J. Zhang, D. Zhang, Z. Tian, J. Wang, K. Liu, H. Lu, D. Tang, J. Meng: *Mater. Sci. Eng.* Vol. A489 (2008), p. 113
- [13] Y.L. Song, Y.H. Liu, S.H. Wang, S.R. Yu, X.Y. Zhu: *Materials and Corrosion* Vol. 58 (2007), p. 189
- [14] H.T. Zhou, X.Q. Zeng, L.F. Liu, Y. Zhang, Y.P. Zhu, W.J. Ding: *J. Mater. Sci.* Vol. 39 (2004), p. 7061
- [15] G. Klaus, J. Eiken, B. Böttger, A. Janz, J. Gröbner, A. Bührig-Polaczek, R. Schmid-Fetzer, in: *Proc. of the 8th Int. Conf. on Magnesium Alloys and their Applications*, edited by U. Kainer, Wiley-VCH Verlag, Weinheim (2010), pp.1217.
- [16] E. Ghali, W. Dietzel, K.U. Kainer: *J. Mater. Eng. Perform.* Vol. 13 (2004), p. 517
- [17] A.M. Gokhale, in: *ASM Handbook*, edited by G.F. Vander Voort, ASM International Materials Park (2004), pp. 428.
- [18] D. Zander, M. Heilig, N. Hort, G. Klaus, A. Buehrig-Polaczek, J. Gröbner, R. Schmid-Fetzer, in: *Magnesium Technology 2010*, edited by S. Agnew, E. Nyberg, W. Sillekens, N. R. Neelameggham, TMS (2010), pp.187.