Correspondence

New insights into the corrosion of magnesium alloys — The role of aluminum

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ABSTRACT

The atmospheric corrosion of several Mg–Al alloys was investigated at −4, 4 and 22 °C. The rate of corrosion increased with increasing temperature and decreasing Al content. Also, the effect of temperature became stronger with increasing Al content. The cast microstructure was found to influence both the average corrosion rate and the temperature dependence of corrosion. The influence of Al on corrosion and on the temperature dependence of corrosion is discussed in terms of the Al enriched layer in the bottom of the surface film and the breakdown of the same layer by chloride ions.

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Environmental degradation is a limiting factor for magnesium–aluminum (Mg–Al) alloys in outdoor applications. Thus, Mg corrosion and Mg alloy corrosion have been the subject of numerous studies during the last two decades [1–13]. There is an ongoing discussion regarding the mechanism of Mg corrosion [1–3]. The effects of environmental variables on the corrosion of Mg–Al systems have been studied [4,5]. Also, there are extensive studies on the role of microstructure in the corrosion of Mg alloys [6–10]. For instance, it has been shown that Mg alloys fabricated by rheocasting (RC) exhibit significantly better corrosion resistance than their counterparts produced by high pressure die casting (HPDC) [11,12]. Despite these research efforts, the influence of temperature on atmospheric corrosion of Mg–Al alloys is largely unexplored. A recent study has shown that while the corrosion of alloy AM50 exhibits a strong temperature-dependence, 99.97% Mg does not [13]. The atmospheric corrosion of Mg–Al alloys at low temperatures is of interest especially in automotive applications. This is because in many regions cars are exposed to severe corrosive conditions during winter, due to the use of de-icing salt. Other important unresolved issues in the atmospheric corrosion of Mg–Al alloys include how exactly Al and chloride (Cl^-) ions influence the protective character of the quasi-passive surface films.

This study addresses the composition of the surface films formed on AZ91D produced by the RC method exposed at 22, 4 and −4 °C. The aim was to shed more light on the role of Al in the corrosion of Mg alloys and on the mechanisms by which the surface film is disrupted by Cl^-. The analyses were performed using high-resolution Auger electron spectroscopy (AES) in a site-specific manner on α-Mg grains and on the

inter-dendritic regions. Details of the exposures are described elsewhere [13]. The corrosion products were analyzed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). We investigated pure Mg (taken from an ingot) as well as several Mg–Al alloys. It should be mentioned that the Fe (~18 ppm) and Ni (~3 ppm) contents of the pure Mg were well below the respective tolerance limits as reported by [14–16]. This was also true for the alloys tested.

The gravimetric results for alloy AZ91D in the RC and HPDC states in Fig. 1a show that the corrosion rate depended strongly on temperature. Also, RC AZ91D exhibited better corrosion resistance than HPDC AZ91D at all three temperatures. The authors have previously discussed the reasons behind the superior corrosion resistance of RC materials [11,12]. The somewhat higher Al content in the α-Mg grains of the RC materials was suggested to be one of the explanations. Interestingly, the results showed that the beneficial effect of microstructure on the corrosion of Mg–Al alloys also depended on temperature (Fig. 1a). Thus, while the average corrosion rate of the HPDC material was ~1.5 times that of the RC alloy at 22 °C, the corresponding factor at −4 °C was ~7.5. To explore how the solidification microstructure affects alloy corrosion at different temperatures, the microstructure and composition of the corrosion products and surface films was subjected to detailed analysis.

The corrosion products formed at 4 and 22 °C were similar (Fig. 1b). $Mg_5(CO_3)_4(OH)_2 \times 4H_2O$ (hydromagnesite) was the dominant corrosion product. Traces of $Mg_5(CO_3)_4(OH)_2 \times 5H_2O$ was also detected. In contrast, at −4 °C, hydroxy carbonates were absent. Instead, two diffraction peaks were observed that belonged to corrosion products but that could not be attributed to any known compound [13]. The peaks appeared irrespective of the presence of NaCl, CO_2 and Al content, implying that it is a compound of magnesium and oxygen and/or

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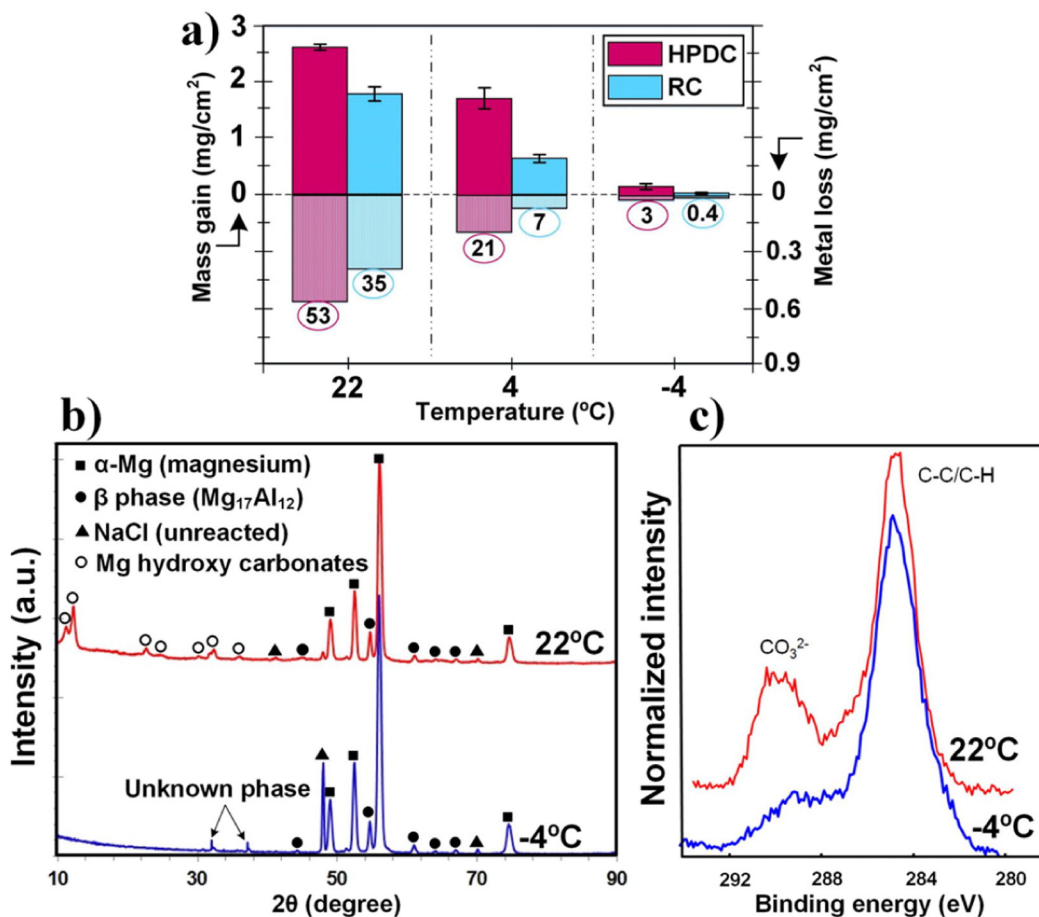**Fig. 1.** (a) Mass gain and metal loss of RC and HPDC AZ91D (after 672 h). Corrosion rates (μm/year) are given beneath the metal loss bars. (b) XRD patterns recorded after the exposures in Fig. 1a at −4 and 22 °C. (c) XPS spectra from alloy AZ91D exposed in the absence of NaCl at −4 and 22 °C after 672 h.

hydrogen, possibly a low-temperature form of Mg hydroxide. The XPS spectra in Fig. 1c show the C1s peak after 672 h in the absence of NaCl at ~4 and 22 °C. The peak at ~290 eV corresponds to carbon in CO_3^{2-}. In line with the XRD results, at 22 °C, a strong CO_3^{2-} peak was detected, while at −4 °C, a much weaker CO_3^{2-} peak was present.

Fig. 2 shows corrosion rates of the alloys. The rate of corrosion decreased strongly with increasing Al content. Pure Mg showed no clear correlation between corrosion rate and temperature. In contrast, alloys exhibited a positive correlation between temperature and corrosion rate. Importantly, the effect of temperature on corrosion was proportional to Al content. In the case of AM20, lowering the exposure temperature from 22 to −4 °C only resulted in a 15% decrease in corrosion rate,

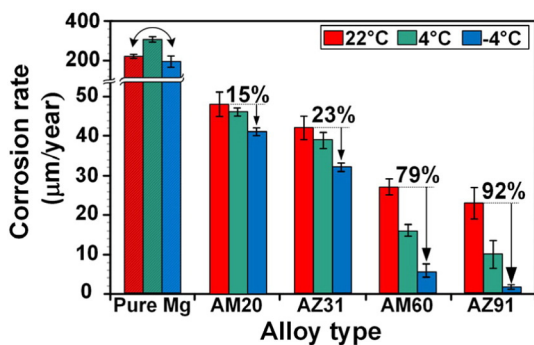**Fig. 2.** Corrosion rate of 99.97% Mg and four HPDC Mg–Al alloys (RH: 95%, CO_2: 400 ppm, NaCl: 70 μg/cm², time: 504 h). The decrease in the corrosion rate from 22 to −4 °C is given as a percentage.

while the same decrease in temperature resulted in a 92% decrease in the corrosion of AZ91D.

It is interesting to note that pure Mg corroded faster than the alloys. This is not consistent with some results presented in the literature. Thus, Liu et al. [16] reports that during immersion in 3% NaCl (aq) solution, the corrosion of Mg alloys was greater than that of high purity Mg. This implies that the relative rate of corrosion of Mg and Mg–Al alloys during exposure to the atmosphere is different from that observed in immersion test conditions. The observed discrepancy is attributed to differences in the corrosion mechanism during atmospheric exposure in the presence of NaCl as compared to NaCl (aq) immersion testing. This topic is beyond the scope of this letter and will be addressed in a future study.

AES compositional depth profiling (Fig. 3) was carried out to investigate the chemistry of the surface films formed on RC AZ91D exposed in a NaCl-free environment. The analyses were performed on the middle of α-Mg grains with ~35 μm diameter containing 3.5 ± 0.1 wt.% Al. In all cases, we reached to the alloy substrate, which exhibited a weak O signal and strong Mg and Al signals (Fig. 3). The surface film formed at −4 °C was much thinner (~22 nm, Fig. 3a) than at 22 °C (~130 nm, Fig. 3c). Irrespective of temperature, the top 5 nm of the surface films had a high atomic percentage of C due to surface contamination. The top part of the film was made of hydromagnesite (in line with the XPS spectra in Fig. 1c). Deeper into the film the O/Mg ratio decreased to about 2, indicating the presence of Mg(OH)₂. The lack of evidence for MgO in the film in Fig. 3 does not rule out the presence of a thin MgO layer at the film/metal interface, as reported by [7,17,18], see also Fig. 4. Small amounts of Al^{3+} were indeed detected in the film. In contrast to the films formed at 4 and 22 °C, the film formed at −4 °C did