Microscopic and surface analyses of corroded Mg alloys

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Abstract. Using optical and SEM microscopic observations and EDX analysis, the corroded surfaces of AZ91, AM50 and AE42 Mg-alloys in 3.5%NaCl were studied at condition of open circuit potential. Different surface composition, morphology, density and characteristics of the surface films were established. The corrosion potential, recorded for 5 days in the case of AE was studied and specific behaviour was observed. EDX analysis established the presence of Mg and Al in the corrosion products of the three alloys and Ce for AE42 and formation of oxides and/or hydroxides of these elements was assumed. A mechanism of dissolution of Mg alloys at OCP condition in NaCl solutions was discussed.

1. Introduction

Magnesium has a lot of advantages [1] and modest cost towards the other metals. Compared with polymers, Mg alloys show superior mechanical properties. The use of magnesium alloys in various industries have been increasing in the past decade, and it is expected that in the coming years this trend will continue. Recently, new Mg alloys with excellent mechanical properties have been reported, [2-6] and their use for industrial purposes appears to be promising.

The most common magnesium die alloy is AZ91. This alloy has extremely good castability and shows high mechanical strength at ambient temperatures. Typical applications include automotive engine parts, computer parts, and parts for handheld tools. Due to the high aluminium content, the alloy has limited ductility and impact strength. To solve this problem AM alloys are developed. They are characterized with better ductility and impact strength. Typical parts made from this alloys include automotive instrument panel subparts, steering wheel cores, seat parts, etc. Extensive efforts have been made to develop magnesium die casting alloys with improved creep properties at temperatures exceeding 120°C. This would open up new applications in manufacturing of elevated temperature-exposed engine parts and automatic transmissions. For this purpose the AE types of alloys have been developed [4] by addition of rare earth (RE) elements. This is an effective way to improve the mechanical properties at elevated temperatures and the corrosion resistance to some degree of magnesium alloys [7, 8].

However, the satisfactory mechanical properties are not enough to enable a magnesium alloy to serve in a practical environment. In fact, the use of Mg alloys remains notably limited because of its high reactivity. Magnesium alloys usually have relatively low corrosion resistance, which is one of the main obstacles that impede the use of magnesium alloys in real world environments. Therefore, corrosion performance is a major issue for research and development of magnesium alloys [6].

The aim of the presented paper was to perform a comparative study of the morphology and composition of the corroded surfaces of three types of Mg alloys – AZ91, AM50 and AE42 as a part of more detailed study of the corrosion properties of these alloys.
2. Experimental
The corrosion environment was a 3.5% NaCl solution with initial pH value 6.7. The specimens were cylindrical (d = 13.5 mm). Before the immersion in the solution the specimens were subjected to the treatment as follows: mechanical cleaning with sand paper (finest grit – 2000); degreasing in an ultrasound bath with ethanol; isolating the side surfaces of the specimens with polymer material and immersion in the corrosion environment up to 120 hours (5 days). Each specimen was immersed individually in a flask with 100 mL corrosion solution. All experiments were performed at room temperature.

Open circuit potential measurements (OCP) were performed using pH/ORP/mV bench meter HI 3220 (Hanna Instruments) with automatic recording and data collection. The potentials were measured and presented versus standard silver electrode (SSE).

The surface appearance was studied by optical observations using inverted metallographic microscope Optika XDS-3MET with built-in camera for digital photography and scanning electron microscopy (SEM) TESCAN Lyra XMU, equipped with EDX spectrometer Bruker GmbH with primary energy 30 keV and detector type XFlash 5010.

3. Results and discussion
At Figure 1 the corrosion potentials of the studied alloys are presented.

![Figure 1](image-url)

Figure 1. Open circuit potential (OCP versus SSE) as a function of time of immersion in 3.5% NaCl.

It is seen, that the potentials of the AZ and AM alloys are almost the same and reach a stable value at about 6 hours, which vary slightly up to end of the study. During the first 5 hours the corrosion potential of AE alloy has similar behaviour as the other two alloys, but has a more negative value (Figure 1a). Additionally, it can be seen that for AE42, the initial potential change in positive direction is sharper.

After 5h immersion the behaviour of the potential of AE is quite different compared to the other alloys. Here, the potential is going to the negative direction and this tendency is keeping up to the end of the experiment. The potential become more negative than the initial corrosion potential (Figure 1b).

Cain and co-workers [9] recently summarized a compilation of corrosion potentials for a number of commercial and experimental magnesium alloys. Results were published for the solution of 0.1M NaCl and the OCP was measured for 10 min prior to polarization testing. The conclusion was, that only minimal changes to the OCP of Mg-alloys were observed. This was contributed to the limited solubility of most elements in crystalline Mg and that Mg is weakly polarisable.

In our study the corrosion media was more concentrated compared to the solution, used in [9]. Data about the prolonged OCP measurement during the whole corrosion testing period were not found.
The results received in our study, for the evolution of OCP are in agreement with the published [9] for the first hours of the experiment in the case of AE. The changing of the OCP with time in negative direction for this alloy is an interesting result, which needs more attention and more detailed study.

The appearance of the corroded surface after 2 and 5 days of immersion, received by optical microscopy, is shown at Figure 2.

**Figure 2.** Corroded surface photographs of studied alloys.

In the first 2 days (48h) the surfaces of AZ and AM are still bright (AZ is rougher), without specific features, while the AE show formation of a darker film on the surface. This appearance can be related to the observed OCP change of AE and the stability of the corrosion potential of AZ and AM in this period of immersion time.

After 5 days (120h) of immersion, the surface appearance of the three alloys is very different. AZ has dark spots, and it is less uniform, AM has bright surface with white residue, while the surface of AE is covered with dense black compact film.

SEM images of the surfaces (Figure 3) confirms the formation of a dense and compact film on the AE and the presence of corrosion products on AZ and AM surfaces with structure quite different compared to AE.

**Figure 3.** SEM images of the corrosion product film on the surface of studied alloys.
EDX analysis of the surfaces before and after the immersion in NaCl are given in Table 1 and Table 2.

Table 1. Chemical (elemental) composition (wt. %) of the surfaces of the studied alloys before the immersion in the corrosion environment.

| Alloy | Mg | Al | Zn | Cu | Fe | Mn | Si | Ce |
|-------|----|----|----|----|----|----|----|----|
| AZ91  | 88.50 | 8.97 | 1.27 | 0.50 | 0.34 | 0.29 | 0.13 | – |
| AM50  | 94.76 | 4.01 | 0.39 | 0.25 | 0.16 | 0.37 | 0.05 | – |
| AE42  | 93.86 | 3.29 | 0.25 | 0.16 | 0.09 | 0.37 | 0.02 | 1.95 |

Table 2. Chemical (elemental) composition (wt. %) of the surfaces of the studied alloys after the immersion in the corrosion environment (3.5% NaCl) for 3 days (72h).

| Alloy | Mg | Al | Zn | Cu | Fe | Mn | O  | Cl | Ce |
|-------|----|----|----|----|----|----|----|----|----|
| AZ91  | 44.95 | 3.33 | 0.89 | 0.36 | 0.21 | 0.27 | 43.71 | 2.84 | – |
| AM50  | 44.92 | 1.80 | 0.49 | 0.26 | 0.19 | 0.16 | 46.34 | 5.14 | – |
| AE42  | 36.28 | 9.82 | 0.45 | 0.52 | 0.13 | 1.40 | 40.42 | 0.06 | 6.53 |

After the immersion in the NaCl solution, in the composition of the corrosion products on the alloy surface, besides the main elements, new elements as O and Cl appear (Table 2). The ratio Mg:O is close to 1:1, which suggest, that the corrosion products on the alloy surface are composed mainly by Mg-oxides and hydroxides.

Moreover, except Mg the results show and the presence of Al in the corrosion products of the three alloys, which means that Al is dissolved during the immersion in the corrosion environment and probably the alloys form Mg(OH)$_2$ and Al(OH)$_3$ precipitates in the solution and the white residue on the specimen surface.

In the corrosion products on AE42 surface, the content of Al is much higher (about 3 times and more) than the one in the other alloy's corroded surfaces and at the same time the Mg and Cl content is the lowest. Additionally, in the AE corrosion product a considerable amount of Ce is detected. The formation of black, dense film on the surface of AE42 is probably due to formation of mixed oxides and/or hydroxides of Al, Ce and Mg. The elements in the film are uniformly spread. The negligible content of Cl on the surface could explain the most compact and dense film on AE compared to the others, bearing in mind the destructive action of chlorine ions on the passive films on the alloy surface.

It is well established [1], that the cathodic reaction during the corrosion of Mg-alloys is water reduction, often also simply termed as HE (hydrogen evolution). The overall corrosion reaction for Mg alloys is:

\[ \text{Mg} + 2\text{H}_2\text{O} = \text{Mg(OH)}_2 + \text{H}_2 \]

It has been shown that the Mg corrosion product exhibits enhanced catalytic activity towards the HE reaction [1]. In other words, the dark corrosion film formed during Mg corrosion at the OCP promotes the evolution of H$_2$ at a faster rate than uncorroded areas on the sample. There is substantial evidence that the dark film is the primary site of cathodic reaction for Mg dissolving at its OCP [10].

The morphology of the attack is directly dependent on the concentration of NaCl in the electrolyte and the amount of Fe present in the material [11]. At a fixed Fe concentration, radial disc-like propagation is exhibited in highly concentrated NaCl solutions whereas lower concentrated NaCl environments lead to a filiform-like attack. This behaviour was attributed to an ohmic effect that influences the current flow in the electrolyte between the net anodes (leading edges) and the net cathodes (dark regions), which are galvanically coupled. A solution with higher NaCl concentration, and thus higher conductivity, allows for more distant galvanic coupling and leads to a radial disk-like attack. On the other hand, solutions with lower conductivity constrain the current flux between net anodes and cathodes, leading to filiform-like tracks that maintain the distance between the galvanically coupled regions at a minimum [11].
According to [11] the introduction of rare earth (RE) elements may lead to the improved surface oxide stability of the alloy, which may help reduce the rate of dissolution of the alloy. One of the important effects of RE on the corrosion resistance of Mg is the so-called “scavenger effect”, i.e., some impurity elements in Mg, such as Fe, severely deteriorates its corrosion resistance, and RE is said to cancel their influence by the formation of intermetallic compounds with the impurities [12]. Meanwhile, the corrosion resistance of Mg mainly depends on the surface oxide film, i.e., the corrosion property of Mg should be affected by RE addition since the surface oxide film changes with the RE addition.

4. Conclusions
A set of optical and SEM microscopic observations of the corroded surface show the different surface composition, morphology, density and characteristics of the surface films. The most compact film is formed on the surface of AE42.

EDX analysis of the alloy surfaces were performed. The presence of Mg and Al in the corrosion products of the three alloys was established and of Ce for AE42. Formation of oxides and/or hydroxides of these elements was assumed. The negligible content of Cl on the surface of AE42 could explain the most compact and dense film on this alloy compared to the others, bearing in mind the destructive action of chlorine ions on the passive films on the alloy surface. A mechanism of dissolution of Mg at OCP condition in NaCl solutions was discussed.

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