Study on corrosion behaviour of AZ91 alloys at different aging time

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Abstract. The current work presents the corrosion behavior of AZ91 magnesium alloys in 0.01M NaCl. 2 different aging time samples were used in this study. It is found that sample with 2 hrs aging time shows a better corrosion resistance as compared to the 4 hrs aging time. It is also showing a significant small amount of hydrogen evolution reaction (HER) during the hydrogen gas collection examination. XRD indicates a few β-Mg17Al12 phase formed at 4 hrs aged samples. This is suggested that the formation of β phase in the alloy were accelerating the corrosion rate due to the galvanic corrosion mechanism.

1. Introduction
Magnesium (Mg) and its alloys are attractive materials for industrial and structural application due to their high strength-to-weight ratios [1–3]. However, the widespread use of Mg and its alloys is currently hindered by poor corrosion resistance, especially in aqueous environments [4–6]. The mechanism of Mg corrosion is atypical as it displays unusual characteristics when compared to other active metals, especially in the case of the cathodic hydrogen evolution reaction. Most popular Mg alloys that had been recently used are AZ90 and AZ91 [7–10]. These are a dual phase alloy with the α-Mg matrix is an Mg-Al-Zn solid solution with the same crystal structure as pure Mg. The corrosion behaviour of these alloys are depends on the chemical composition of its phases [11–15]. Furthermore, the formation oxide layers Mg(OH)2 and MgO significantly affect the hydrogen evolution reaction of these alloys. Therefore, researchers have been interested in understanding the influence of Mg oxide layers to the alloys corrosion behaviour [15–19].

Unfortunately, the current state of knowledge of the corrosion behaviour of these two main phases is not sufficient to allow understanding of the corrosion behaviour of the AZ90 alloy. On some points, there are even contrary explanations for the same phenomenon. Few researchers believed that the β phase in AZ90 or AZ91 acts as an inert corrosion barrier, so that the presence of this phase improves the corrosion resistance. They found that aged AZ80 containing β had a corrosion rate lower than that of solution treated AZ80 without β [4, 20]. In contrast, few other researchers [21, 22] had proposed that the presence of β phases increases the corrosion rate by galvanic corrosion between the intermetallic β and the magnesium alloy matrix (α-Mg). In this particular view, the presence of β phase in an alloy would decrease the corrosion resistance of the alloy. Other than that, few researchers
had found decreasing of corrosion resistance in Mg-Al alloy after aging above 130°C. This is might due to the precipitation of additional β phase along the grain boundaries. For the α-Mg phase, some were reported that corrosion resistance could be improve with the increasing of Al content. Conversely, Lunder et al., [23] had found an increasing of anodic activity in Mg-Al alloys as the Al content was increased. Therefore, it is essential to clarify the roles each phase’s presents in microstructures to improve the corrosion resistance of Mg-Al alloys, especially in AZ90 and AZ91.

In this study, the corrosion behaviour of AZ91 samples has been thoroughly studied. This is in order to have a fundamental knowledge in how different phases presented in samples will affect the corrosion behaviour of aged AZ91 at different aging time [24-26].

2. Methodology

2.1 Sample Preparation

The AZ91 samples were formed by compaction of metal powder with the composition of 90% Mg, 9% Al and 1% of Zn. The powders were carefully mixed for 20 hrs to reach homogeneity. The mixed powders were compact at the pressure of 400MPa to form a solid pallet of AZ91. Then samples were sintered at 450°C for 2 hrs. After 2 hrs of cooling, samples were sintered again at 415°C temperature for 2 hrs and quenching into the water solution. Both of the samples then were aged at 175°C temperature for 2 different times, 2 and 4hrs. This is considering as the parameter that would be study in the paper. Samples then were characterised using X-ray Diffraction method.

2.2 Hydrogen Gas Collection

The hydrogen gas collection method was carried out to estimate the hydrogen gas evolve from the exposed surface of the samples. First, samples were cut into a square of 1cm x 1 cm exposed area. Then samples were mounted and grind up to 1200 grit sand paper. Samples were immersed in 0.01M NaCl for 48 hrs. The hydrogen evolved during the immersion time was collected in a burette by a funnel above the corroding sample’s surface.

2.3 Potentiodynamic Polarisation

Both of the aged samples were ground to a 1200 grit finish again than carefully cleaned using ethanol and dried before electrochemical testing. The samples were polarised from -2.2V to -1.2V SCE in 0.01M NaCl. With the exposed area of 1cm², samples works a working electrode, saturated calomel electrode (SCE) as a reference electrode and Pt-mesh as a counter electrode to complete the three-electrode electrochemical set-up. Testing was carried out via potentiostat with the Nova software.

2.4 Scanning Electron Microscopy (SEM)

The morphology of the corroded surface was examined by the Scanning Electron Microscopy (SEM) JSM 6460LA (JEOL, JAPAN). Samples were characterised by 2 different magnifications, 100x and 500x via secondary electron imaging (SEI) mode.

3. Result and discussion

The presence of phases in AZ91 had been confirmed by XRD. Both of the ground and polished samples were analysed using XRD before undertakes any electrochemical test. As previously been found, the main phases that will be found in both of the AZ91 (aged for 2 hrs and 4 hrs) are α-Mg and β-Mg_{17}Al_{12}. However, as can be seen in the Figure.1, the few peaks that represent β-Mg_{17}Al_{12} in 4 hrs aged AZ91 is not present in 2hrs aged AZ91. This is indicates that, the β-Mg_{17}Al_{12} phases had formed more in 4 hrs aged AZ91 samples. It is believed that the phase is distributed along the grain boundaries. In 2 hrs aged AZ91 sample, the main peak of both α-Mg and β-Mg_{17}Al_{12} phases can be clearly seen on the graph.
The typical potentiodynamic polarisation response of AZ91 samples tested is presented in Figure 2. The 2 hrs aged AZ91 presents slower anodic kinetic as compared to 4hrs aged AZ91, which indicates that anodic dissolution of 4hrs aged samples is actively taking place when sample were polarised above the OCP. Other than that, the corrosion rate of 4 hrs aged sample is slightly higher than 2 hrs aged sample. This is showing that, longer aging time for AZ91 deliver insignificant effect of corrosion rate towards the samples. However, on the cathodic kinetic, when polarised at higher potential, 2 hrs aged AZ91 does intensify the rate of reactions. Consequently, it became slower as the potential drop to -2.0V_{SCE}. The rate of cathodic reaction for both samples became similar at this potential.

![Figure 1. The XRD for AZ91 aged at two different time (2 hrs and 4 hrs).](image)

![Figure 2. Potentiodynamic polarisation data in 0.01 M NaCl for AZ91 at different aging time (2 hrs and 4 hrs).](image)
Figure 3. Hydrogen collection of AZ91 (2 hrs and 4 hrs aged) following 48 hrs immersion at OCP in 0.01 M NaCl.

When both of the samples were tested using the hydrogen gas collection, significant hydrogen gas had been found evolved from the 4 hrs aged sample surface (Figure 3). This is indicates that a very high hydrogen evolution is taking place towards the 4hrs aged sample. Meanwhile for 2 hrs aged sample, the hydrogen gas could only be seen after 24hrs of immersion in 0.01 NaCl solutions. Less hydrogen gas collected in 2 hrs sample indeed reveals that the shorter time of aging will suppress the cathodic reaction upon the AZ91 and longer time of aging will intensify the cathodic reaction of AZ91. Whilst, it may be obvious, we make the point here that, presence of more $\beta$-Mg$_{17}$Al$_{12}$ phases in 4hrs aged AZ91 will accelerates the cathodic reaction caused by the galvanic corrosion between the $\beta$-Mg$_{17}$Al$_{12}$ phases and the $\alpha$-Mg phases.

From the SEM analysis (Figure 4 (a) and (b)), 2hrs aged AZ91 show a relatively flaky corroded surface. The formation of oxide layers are scattered on the 100x magnification image. The non-corroded surface still can be seen on the figure as crack area, which is believed as initial oxide layer that formed before the immersion. However, the corroded area (Figure 4 (b)) which covered by oxide layers can be seen as a dense surface. This could be the reason why the anodic reaction of the sample was slower compared to the 4hrs aged sample. Meanwhile for 4 hrs aged AZ91 (Figure 5 (a) and (b)), the whole surfaces looks lumpy. It is believed that, the whole surface has been covered by the Mg oxide layers (MgO and Mg(OH)$_2$) which can be seen like amorphous layer deposited on the surface.

Figure 4. a) SEM image of corroded 2 hrs aged AZ91 at 100x magnifications; b) SEM image of corroded 2 hrs aged AZ91 at 500x magnifications.
Figure 5 a) SEM image of corroded 4 hrs aged AZ91 at 100x magnifications; b) SEM image of corroded 4 hrs aged AZ91 at 500x magnifications.

It is also thick and light, which could be the reason of higher cathodic reaction and hydrogen evolution reaction during immersion.

4. Conclusion
The corrosion rates of 2 hrs aged AZ91 alloys determined from the potentiodynamic polarisation slightly decreased as compared to the 4 hrs aged sample. However, the hydrogen evolution rate of 4hrs aged sample determined from hydrogen gas collection method shows very high rates compared to 2 hrs aged sample. This result could be attributed to the formation of more secondary phase β-Mg17Al12 after longer time of aging. The abundantly presence of β-Mg17Al12 phase which content Al element would be the causes of galvanic corrosion of AZ91 during the immersion.

5. References
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