The Influence of Hot Forming on the Microstructure and Corrosion Behaviour of AZ31B Magnesium Alloys

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ABSTRACTS

The influence of the hot forming process of AZ31B wrought and twin roll cast (TRC) magnesium alloy sheets on the microstructure and corrosion behaviour have been evaluated. The corrosion behaviour was investigated by hydrogen evolution experiments in chloride-containing solution. Filiform-like corrosion was predominant attack to the AZ31 magnesium alloys, as observed by in-situ corrosion observation. The intermetallic particle existence and grain structure significantly influenced the corrosion rate. The dendritic structure of the as-cast TRC alloy was severely attacked, revealing that the as-cast alloy was highly susceptible to corrosion. The presence of twins in wrought alloy was found to act as a corrosion barrier, while the increase in grain size showed the high corrosion rate of the alloy.

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1. INTRODUCTION

Magnesium is the lightest of all engineering metals and has the potential to promote energy efficient transportation. Specifically, magnesium alloys are characterised by their high strength-to-weight ratio, high thermal conductivity, good vibration damping, good castability, recyclability and biocompatibility. Magnesium and its alloys are also known to exhibit poor formability in conventional forming operations at ambient temperatures that is related to the hexagonal close packed (HCP) structure, and low corrosion resistance in most environments. Extensive work by (Song & Atren, 1999; Ambat et al., 2000; Witte et al., 2006; Pardo et al., 2008; Song & Xu, 2012) has been carried out to investigate the corrosion performance, but the mechanistic understanding is still the subject of discussion.
Recently, the utilisation of efficient twin roll casting (TRC) in producing magnesium alloy sheets has expanded (Watari et al., 2007; Park et al., 2007; Bayandorian et al., 2012). TRC combines casting and rolling to produce the final products and provides much faster solidification. This cost-effective one step process can result in grain refinement and homogeneity in the microstructure, with reduced segregation.

The formability of magnesium alloys is relatively high at elevated temperature, which activates the non-basal slip system. Thus, hot forming technique has been developed, that is intended to improve the formability of magnesium alloys, as well as to improve the mechanical properties (Garrett et al., 2005; Wang et al., 2011; Alias et al., 2017; Máthis et al., 2018). The process involves solution heat treatment at elevated temperature, stamping and rapid cooling by cold die quenching. The process can change the microstructure by modifying the grain structure and intermetallic particle distribution, and also changing the densities of twins and dislocations. Consequently, the process is also expected to influence the corrosion properties. The present work considers the microstructure modification by the hot forming process on the corrosion behaviour of AZ31B magnesium alloys.

2. Experimental

2.1. Material and method

Two types of AZ31B magnesium alloy were used in the present work, namely wrought AZ31B-H24 (Al 2.78 wt%, Zn 0.89 wt%, Mn 0.41 wt%, Fe 0.03 wt%, Si 0.01 wt%, Cu 0.02 wt%, Mg Bal) and twin roll cast (TRC) AZ31B (Al 3.43 wt%, Zn 0.98 wt%, Mn 0.3 wt%, Fe 0.02 wt%, Si 0.03 wt%, Cu 0.02 wt%, Mg Bal) in the form of sheet. The sheets underwent a hot forming process, by heating in a furnace to temperature of 450°C, with immediate transfer to the die, stamping at a rate of 250 mm/s and rapid cooling by cold-die quenching. The hot forming process in this paper is termed HFQ. The schematic diagram of the HFQ process and its specimen image are shown in Figures 1(a) and (b).

For microstructural characterisation, the specimens were mounted in resin, ground with SiC paper and mechanically polished with diamond paste to 0.25 µm finish. The specimens were degreased ultrasonically in ethanol and quickly dried in a stream of cold air. The polished specimens for optical microscopy were etched for 20 s in picral etchant, composed of 6 g picric acid, 5 ml acetic acid, 10 ml distilled water and 100 ml ethanol. The alloy microstructure was characterised by optical microscopy and scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) for elemental composition. Grain and intermetallic particle size distributions were determined using ImageJ and OriginPro 8.5 software.

To prepare specimens for the hydrogen evolution experiment, the specimens were immersed for approximately 15 min in hot chromic acid solution for cleaning and removing any oxide layer present due to the heat treatment. The specimens were then immersed in a beaker of 3.5 wt% NaCl solution. A funnel and burette were used to collect the hydrogen gas evolved once the reaction started. After testing, the corrosion morphology was examined using scanning electron and optical microscopies.
3. RESULTS AND DISCUSSION

3.1. Microstructure of as-received and HFQ alloys

The typical microstructures of the as-received AZ31B-H24 wrought magnesium alloy and AZ31B twin roll cast (TRC) alloy are shown in Figures 2(a) and 3(a). For the as-received wrought alloy, the microstructure consists of the α-Mg matrix, with high density of twins created due to deformation during hot rolling and the work hardening process (H24), and a bimodal distribution of intermetallic particles. The common intermetallics in this alloy are Al₈(Mn,Fe)₅ particles, with random particle size distribution in the range of 1-25 µm as observed by scanning electron microscopy. It has been stated in the literature that Mn is essential in improving the corrosion resistance as well as controlling the detrimental influence of iron (Matsubara et al., 2013).

After the hot forming process at 450°C, the microstructure of AZ31B-H24 wrought alloy exhibits equiaxed grains, with a changed average grain size to about 13 µm, with almost no twins evident, as shown in Figure 2(b). It is generally known that the crystallographic defects such as grain boundaries, dislocations and twins are preferred sites for corrosion due to their higher electrochemical activities (Song & Xu, 2012). However, it has been observed by (Aung & Zhou, 2010) that the grain boundaries and twins act as corrosion barriers for Mg alloys. The smaller-size grain creates more grain boundaries and twins which lead to increased anodic dissolution. Since the as-received AZ31B-H24 alloy contains a high density of twins, then the twins are more likely to influence the corrosion behaviour compared with the grain boundaries. The Al₈(Mn,Fe)₅ particles are randomly distributed, with diameter up to 25 µm, with relatively little reduction in particle volume fraction after hot forming due to the short duration of heat treatment during the HFQ process. It is known that the Al₈(Mn,Fe)₅ particles are cathodic with respect to the matrix and, hence, influence the corrosion of the matrix. Further, since the particles volume fraction have only been reduced slightly, then it is suggested that the corrosion resistance of the wrought HFQ alloy will not be altered.
The microstructures of the AZ31B TRC magnesium alloy (Figures 3(a)) consist of a fully dendritic structure with sizes of ~200 µm and β-Mg₁₇Al₁₂ networks that are continuously distributed along the dendritic boundaries. Whilst, the HFQ AZ31B TRC alloy revealed equiaxed grains and dendritic features observed by optical microscopy (Figure 3(b)). The β-Mg₁₇Al₁₂ particles (Figure 3(c)) found to change from continuously to randomly distributed at the dendritic boundaries after HFQ. Some of the particles disappeared after the hot forming process with only the grains remain segregated in the dendritic boundaries. A bimodal distribution of Al₈(Mn,Fe)₅ particles was also evident in the HFQ AZ31B TRC alloy, in which the smaller size (<1 µm) Al₈(Mn₅) particles, without any trace of Fe, are distributed along the interdendritic structure, whilst the larger size (~9 µm) Al₈(Mn₅,Fe)₅ particles were randomly distributed in the matrix.

Aluminum is generally known to have a ‘dual role’ effect on the corrosion resistance depending on the distribution of second phase particles. Song & Atrens (1999) noted that β-Mg₁₇Al₁₂ particles might act as galvanic cathodes and accelerate the corrosion rate of the α-matrix, if it forms in random distribution. However, the particle which forms in a continuous network distribution could act as corrosion barrier on the alloy matrix. In the present case, it is clear that the β-Mg₁₇Al₁₂ particles in the HFQ AZ31B TRC alloy are randomly distributed in the matrix and, hence, they may act to accelerate the corrosion rate.

Figure 2. Optical images of: (a) as-received AZ31B-H24 Mg wrought alloy; (b) HFQ AZ31B-H24 sheet with bimodal distribution of Al₈(Mn₅,Fe)₅ particles.

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3.2. Corrosion behaviour

In order to obtain the influence of alloy microstructure on the corrosion rate, the hydrogen evolution experiment was carried out for 7 days. As shown in Figure 4, the hydrogen evolution rate for both alloys increased from day 1 to 7, and displays a sigmoidal trend. It shows a slower hydrogen evolution rate from day 1 to day 2 and displayed a higher rate from day 2, particularly for the TRC alloys. During the hydrogen evolution experiment, the reaction started with hydrogen bubbles formed on features on the exposed specimen surface, with filiform-like corrosion attack of the matrix and the hydrogen gas stream eventually evolved during the attack. The corrosion filament linked with the adjacent filament and spread over the entire surface. The HFQ AZ31B TRC alloy reacted more aggressively compared with the HFQ wrought alloy throughout the experiment and it is obvious from Figure 4 that the TRC alloys were highly corroded compared with the wrought alloys.

The severe corrosion attack on the HFQ TRC alloy compared with the as-cast TRC alloy is believed to be influenced by the random distribution of \( \beta\)-Mg\(_{17}\)Al\(_{12} \) particles, which serve as cathodes that accelerate the corrosion and the plastic deformation. The more severe attack on TRC alloys compared with wrought alloys is probably associated with the grain structure of the TRC which presented dendritic features. The filiform-like attack could resemble the dendritic features, which displayed larger and deeper localised attack than the equiaxed grains.
4. CONCLUSION

The hot forming quenching process significantly influenced the corrosion behaviour of wrought and TRC AZ31B Mg alloys. The as-received AZ31B-H24 alloy showed higher corrosion resistance compared with the HFQ AZ31B-H24 alloy. The HFQ AZ31B TRC alloy displays equiaxed grains, with dendritic features, a random distribution of $\beta$-Mg$_{17}$Al$_{12}$ and Al$_8$(Mn,Fe)$_5$ particles. The intermetallic particles acted as cathodes and accelerated the corrosion of the alloy. Filiform-like corrosion is the predominant form of corrosion on both alloys, with the corrosion appearance resembling the grain and dendritic features. The HFQ AZ31B TRC alloys were found to be the most highly corroded alloys, which correlated with the dendritic features and the distribution of $\beta$-Mg$_{17}$Al$_{12}$ and Al$_8$(Mn,Fe)$_5$ particles.

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6. AUTHORS’ NOTE

The author(s) declare(s) that there is no conflict of interest regarding the publication of this article. Authors confirmed that the data and the paper are free of plagiarism.

7. REFERENCES


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