Atmospheric corrosion behavior of field-exposed magnesium alloys: Influences of chemical composition and microstructure

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ABSTRACT

Ten kinds of magnesium alloys with various chemical compositions and/or microstructures were exposed to actual atmospheric environments for three years, and the influences of chemical compositions and microstructures on atmospheric corrosion behavior of magnesium alloys were investigated. The results showed that the atmospheric corrosion resistance of magnesium alloys generally increased with the Al content in the alloys, but intermetallic phases had a considerable influence on the corrosion resistance. Grain refinement improved the corrosion resistance of magnesium alloys. It was also found that atmospheric corrosion rate increased with exposure time, and this phenomenon was explained in the present work.

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1. Introduction

Magnesium alloys have the lowest density among structural metallic-materials, which makes them attractive for automotive and aerospace industries where weight is of importance. However, their application is limited to a single-component level mainly due to low strength, poor formability and corrosion resistance [1]. In order to widen the range of application of magnesium alloys, many efforts have been made to improve not only the mechanical properties but also the corrosion resistance of magnesium alloys [2–5]. Most of the previous works have been attempted to study the corrosion behavior of magnesium alloys by means of immersion test in saline solution and/or salt spray test, aiming an insight into the effects of chemical compositions, impurities and microstructures on the corrosion resistance of magnesium alloys as well as corrosion mechanisms [6–31]. It has been understood that the poor corrosion resistance of magnesium alloys is attributed to the less-protective hydroxide film formed on magnesium surface and the internal galvanic corrosion caused by intermetallic phases or impurities [6,7]. The surface film is quasi-passive and its passivity is affected by the alloying elements, especially Al content in the magnesium alloys [8,9]. In the presence of carbon dioxide, the anti-corrosion ability of surface film is improved due to the formation of carbonate and/or hydroxide carbonate films that are more protective than

hydroxide film [10]. The impurities known as Fe, Ni, Co and Cu are detrimental [11], and a great deal of effort has been made to reduce the impurities to the level within their tolerance limits such that the current commercial magnesium alloys have a much higher corrosion resistance than those at earlier stage [12,13].

The influence of intermetallic phases on the corrosion behavior is comparatively complex and dependant on their type, size and morphology. While almost all the intermetallic phases exhibit nobler potentials than magnesium matrix, their potential difference with magnesium matrix is various for different phases [14,15]. Many researches show that β phase can act either as a barrier to inhibit the corrosion or as a galvanic cathode to accelerate the corrosion of magnesium alloys [16,17]. The β phase is expected as a barrier when there is a small grain size and relatively large β phase fraction, and more importantly the β phase is in the form of a continuous network along Mg grain boundaries [16]. In contrast, microgalvanic corrosion is readily accelerated as the β phase is agglomerated and separately distributed in the Mg matrix of coarse grains [18]. Other intermetallics than β phase are found to be harmful by promoting the microgalvanic corrosion [19,20], but finely distributed intermetallic particles seem to be innocuous to corrosion resistance [21–23].

The influence of grain size on the corrosion behavior of magnesium alloys has not yet been determined [24–27], but the great majority of previous works show that the corrosion rate of fine-grained magnesium alloys is lower that that of coarse-grained magnesium alloys [28–31]. A reasonable explanation of the beneficial effect of grain refinement is that the increased grain boundary

density may help compensate for oxide/base metal mismatch by decreasing compressive stress that otherwise would lead to cracks in the oxide film [24], and the more stable oxide film on the surface of magnesium alloys with finer grains may account for the improved corrosion resistance [24,31].

As compared to the research on aqueous corrosion of magnesium alloys, the works on atmospheric corrosion of magnesium alloys are comparatively less and insufficient, and most of them are performed in simulated atmospheric environment in laboratory [32–37]. Laboratory tests reveal that the atmospheric corrosion rate of AM50 and AZ91D magnesium alloys becomes larger when either temperature, relative humidity (RH) or the amount of NaCl is increased [33]. The surface film of magnesium alloys has a protective effect, to some extent, for AZ31 and AZ61 alloys in a simulated atmosphere without chlorides [36], but it is less protective in the environment where chlorides are present in the atmosphere. Similar to the aqueous corrosion of magnesium alloys, microstructure is also important to the atmospheric corrosion of magnesium alloys. The role of β phase seems to be the same for the atmospheric corrosion and aqueous corrosion of magnesium alloys [37,16,18], and fine-grained AZ31B magnesium alloys have a higher atmospheric corrosion resistance than coarse-grained AZ31B alloys [38]. However, there is little information about the influence of other intermetallics than β phase on the atmospheric corrosion of magnesium alloys.

Since atmospheric corrosion is strongly affected by environmental factors and/or climatic parameters, the field test is of special importance for the evaluation of atmospheric corrosion resistance of magnesium alloys. Recently, there are several reports on the filed-exposure test results of magnesium alloys [38–42], but the exposure duration in these works is comparatively short, and the magnesium alloys used in the exposure test are few, so that it is hard to obtain comprehensive knowledge from these works. In this study, ten kinds of magnesium alloys, including three AZ31B and two AM60 alloys with various grain sizes, three AMX602 and two AZ91D alloys prepared by different processing methods, were exposed in various fields for three years, and the atmospheric corrosion behavior of these alloys was investigated. The purpose of this work is to achieve a comprehensive understanding of atmospheric corrosion behavior of magnesium alloys in real atmospheric environment.

2. Experimental details

2.1. Materials

ASTM-specified AZ31B, AM60, AZ91D alloy ingots were used in the present work. AMX602 alloy ingot, a non-ignitable magnesium alloy ingot made by adding about 2 mass% Ca to AM60 alloy, was also employed to investigate the effect of Al–Ca intermetallic phase on atmospheric corrosion behavior of magnesium alloys. Ten kinds of magnesium alloys, including three AZ31B (marked as AZ31B-1, AZ31B-2 and AZ31B-3), two AM60 (marked as AM60-1 and AM60-2), three AMX602 (marked as AMX602-C, AMX602-E and AMX602-S) and two AZ91D alloys (marked as AZ91D-C and AZ91D-E) were prepared from AZ31B, AM60, AMX602 and AZ91D alloy ingots, respectively, by various manufacturing processes. The ten magnesium alloys are summarized in Table 1, where chemical compositions of AZ31B, AM60, AMX602 and AZ91D alloy ingots are presented together with manufacturing processes of the magnesium alloys.

AZ31B-1 alloy was produced by hot extrusion of AZ31B billets machined directly from AZ31B ingots. The hot-extrusion was conducted at an extrusion ratio of about 21, extrusion ram speed of $0.5\,mm\,s^{-1}$ and extrusion temperature of 623–673 K. The

magnesium alloy plates made by hot extrusion were 75 mm in width and 4 mm in thickness. AZ31B-2 alloy was manufactured by roll compaction process (RCP), a severe plastic deformation process, and hot extrusion. The details of RCP were described elsewhere [3,4,31,43]. For the preparation of AZ31B-2 alloy, AZ31B ingots were cut into plates of 210 mm in length, 50 mm in width and 4.5 mm in thickness, rolled to sheets of 0.7 mm in thickness once by a twin-roller at room temperature, and subsequently crushed to flakes of about 5 mm in diameter by a granulator. Then the flakes were passed through a strong neodymium magnet bar, and the flakes contaminated by Fe were removed. The above RCP was conducted 1 time. The severely deformed flakes were collected and consolidated to billets, and then hot-extruded to plates using the same extrusion parameters as AZ31B-1 alloy. Since AZ31B-2 alloy experienced severe plastic deformation process, the grain size of AZ31B-2 alloy was much smaller than that of AZ31B-1 alloy. The AZ31B-3 alloy was made using the same manufacturing process as AZ31B-2 alloy, but the RCP was conducted 5 times. In the RCP of 2–5th time, the flakes were compressed by the twin-roller at room temperature to form thin sheets, which were then crushed to flakes again by the granulator. Because AZ31B-3 alloy had more plastic strain than AZ31B-2 alloy, the grain size of AZ31B-3 alloy was smaller than that of AZ31B-2 alloy. AM60-1 and AM60-2 alloys were prepared using the same manufacturing processes as AZ31B-1 and AZ31B-2, respectively. AM60-2 alloy had much smaller grain size than AM60-1 alloy. It should be noted that Fe contamination was removed after RCP, and thus Fe content in these magnesium alloys was at the same level as that of their ingots.

AMX602-C alloy plates were fabricated by gravity cast, followed by machining. AMX602-E alloy was produced by hot extrusion using the same parameters as AZ31B-1 alloy. AMX602-S alloy was prepared by spinning water atomization process (SWAP) and hot extrusion. Firstly, the AMX602 alloy ingot was atomized by the spinning water atomization process, in which gas atomization was combined with water atomization to produce an extremely high solidification rate of about 106 K/s, which resulted in powders with fine microstructures and super saturation of alloying elements [23]. Then the atomized powders were collected and consolidated to billets and subsequently hot-extruded to plates using the same parameters as AZ31B-2 alloy. It should be noted that the chemical compositions of AMX602-C, AMX602-E and AMX602-S alloys were almost the same, but microstructures were greatly different.

AZ91D-C alloy plates were prepared by gravity cast and machining, like AMX602-C alloy plates. AZ91D-E alloy was made by hot extrusion using the same extrusion parameters as AZ31B-1 alloy. The chemical compositions of AZ91D-C and AZ91D-E were the same, but microstructures were different.

2.2. Microstructure characterization

The microstructures of the ten magnesium alloys used in this work were characterized by using an optical microscope, scanning electron microscope (SEM, JEOL: JSM-7000F) and transmission electron microscope (TEM, JEOL: JEM-4000EX, operating at 300 kV). The specimens for microstructure characterization were cut from magnesium alloy plates, with the observation plane perpendicular to the extrusion direction for those extruded alloys. Specimens for optical microscopy and scanning electron microscopy were ground finally with 4000 grit emery paper, polished using 0.25 μm diamond paste and then etched with a solution consisting of 10 g picric acid, 175 ml ethanol, 25 ml acetic acid, and 25 ml distilled water. Thin foils for TEM observation were prepared using a focused ion beam instrument. Energy-dispersive X-ray spectroscopy (EDS) and electron diffraction were used to analyze the intermetallic phases in these alloys.