Corrosion Science 77 (2013) 143–150

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Impurity control and corrosion resistance of magnesium–aluminum alloy

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ARTICLE INFO

Article history:
Received 18 February 2013
Accepted 25 July 2013
Available online 2 August 2013

Keywords:
A. Alloy
A. Magnesium
A. Iron

ABSTRACT

In the present study, the corrosion behavior of AXJ530 magnesium alloy with different iron and manganese contents is investigated in 3.5 wt% sodium chloride solution in order to tailor the tolerance limit of Fe impurity in the magnesium alloy. Through a comprehensive phase diagram calculation and corrosion evaluation, the mechanisms for the tolerance limit of Fe in magnesium alloys are discussed. The study adds a new dimension to controlling the Mg alloy impurity in terms of alloying composition design and casting conditions.

1. Introduction

Magnesium alloys are promising materials in the automobile and aerospace industries due to their low density and high strength-to-weight ratio. However, their poor corrosion performance [1–10] limits their practical applications.

Magnesium is extremely sensitive to impurity elements: Fe, Ni, Cu and Co [1,11,12] in terms of the corrosion performance. There is a tolerance limit for each of the impurities in magnesium or its alloy. The corrosion of a magnesium alloy is usually insignificant if the concentrations of these impurities are below their tolerance limits, whereas the corrosion rates will substantially increase after the impurity concentrations exceed the tolerance limits, such an increase can sometimes even exceed 100 fold, e.g., in a non-linear fashion. Liu et al. [13] summarized the corrosion rates of various magnesium alloys immersed in salt water. After a comparison of these alloys' chemical compositions, they found that the corrosion rates of these magnesium alloys were typically below 10 mm/y (millimeter per year); however, if the magnesium and magnesium alloys were contaminated with Fe impurity (usually above 40 weight ppm), the corrosion rates were usually above 20 mm/y, and in some cases, greater than 200 mm/y. Therefore, a very simple surface cleaning process can efficiently remove the Fe contamination on a commercial magnesium alloy and lead to a dramatically decreased corrosion rate [14–17]. The impurity tolerance limits are different for different impurities. The tolerance limits of Fe, Ni and Cu are 170 weight ppm, 5 weight ppm and 1000 weight ppm, respectively [11,12].

Other elements have an influence on the tolerance limit of Fe. For example, aluminum alloying decreases the iron tolerance limit, but manganese addition can increase it [13]. Riechek, Hillis, Mercer, et al. studied the tolerance limits of impurities in magnesium alloys AZ91 [18], AM60 [19], AS41 [20] and AE42 [21]. Their results indicated that the tolerance limits of Ni and Cu are independent of the Mn content, but the Fe tolerance limit is closely related to the Mn content, and the corrosion rate is dependent on the weight ratio of the Fe content to the Mn content. Their experimental results revealed that there is a critical Fe to Mn weight ratio, above which the corrosion rate of magnesium alloy sharply increases as the Fe/Mn wright ratio increase. The critical Fe/Mn weight ratio ranges from 0.010 to 0.032, depending on the alloy type [18–21]. These critical Fe/Mn weight ratios have now been widely cited as an ASTM standard [22], although there is one report [23] that states the critical Fe/Mn weight ratios in the AM50 magnesium alloy can be set between 0.0072 and 0.0101 while in the AM60 magnesium alloy it can be between 0.007 and 0.232.

Although the Fe/Mn weight ratio criterion works very well in industrial corrosion control practice, there are a few questions about this interesting phenomenon from a scientific point of view. First, why is there a sudden change when the Fe/Mn weight ratio reaches a certain value? Hillis et al. offered several possible explanations [19,20], but none of them have been experimentally proved. Second, why is this critical Fe/Mn weight ratio different in different magnesium alloys? Third, what metallurgical factors determine this ratio value?

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http://dx.doi.org/10.1016/j.corsci.2013.07.037

These questions have not been well answered until recently Liu et al. [13] tried to explain the Fe/Mn weight ratio based on calculated Mg–Fe phase diagrams using Pandat software, which is a software package for calculation of phase diagrams and thermodynamic properties of multi-component alloys [13]. The calculated Mg–Fe binary phase diagram indicated that during non-equilibrium cooling (casting solidification), the magnesium melt containing less than 180 weight ppm Fe would solidify to a single α-Mg phase with Fe in a supersaturated solid solution in the magnesium lattice. A magnesium melt or casting containing more than 180 weight ppm Fe would produce a separate iron-rich phase during cooling and solidification [13]. If this phase is an efficient cathode, it will accelerate the alloy corrosion due to its micro-galvanic coupling to the magnesium matrix. In this case, the tolerance limit of Fe in pure magnesium corresponds to the maximum content of Fe dissolved in cast magnesium above which a Fe-rich phase will precipitate from the melt before final solidification. Therefore, for cast pure magnesium or non-equilibrium magnesium, the tolerance limit of Fe is predicted to be 180 weight ppm, which is in agreement with the 170 weight ppm stated in literature [11,12]. In the case of Mg–Al–Fe–Mn melts, the calculation for the Mg–Al–Mn–Fe system was agreed with previous studies [18–20]. However, the calculated Fe–Mn curve gives a slope of 0.143 in the isothermal section at 651 °C from the Mg–5 wt% Al–Mn–Fe phase diagram. This is much higher than the 0.01–0.032 values stated in the literature [18–20].

In the phase diagram calculation, both Al_8Mn_5 phase and Fe-rich phase can be obtained. The Fe rich phase is a strong cathode to the Mg matrix and can cause high corrosion rates, while the Al_8Mn_5 phase is a relatively passive phase. The Al_8Mn_5 phase precipitates as the Fe rich phase dissolves. In this process, the Fe content may transfer into the Al_8Mn_5 phase and become inactive to the Mg matrix. Many studies [24–26] have mentioned the presence of Fe in the Al–Mn intermetallic. Liu et al. even observed a tiny Fe-rich area using back scatter electron imaging in Scanning Electron Microscopy (SEM) [13]. However, no Fe was detected at all in other work [27–29]. With the help of Scanning Kelvin Probe Force Microscopy (SKPFM) techniques, the Volta potential difference of the Al_8Mn_5 phase relative to the magnesium matrix has been scanned [15,24,30]. It was reported that the potential of Al_8Mn_5 is only about 200–250 mV more positive than that of the Mg–Al matrix [15]. However, a much higher average potential value (250–350 mV) and standard deviation (90 mV) for this intermetallic than those of $Mg_{17}Al_{12}$ (potential value 60–150 mV, standard deviation 20 mV) have also been reported in other studies [24,30]. This inconsistency in potential is possibly caused by a variation of the Fe content in the intermetallic particles. Nevertheless, the maximum Volta potential difference between the Al_8Mn_5 phase and the magnesium matrix is around 500 mV, much smaller than that between Fe and Mg, which is about 2000 mV. Therefore, a Fe-rich phase would be a strong cathodic phase that can significantly deteriorate the corrosion resistance of the magnesium alloy, rather than a Fe-free Al_8Mn_5 phase. For example, a recent study [23] showed that inclusions were present within magnesium alloys with compositions of 40–80 wt% Al, 20–60 wt% Mn and 0–10 wt% Fe, and corrosion preferentially occurred around inclusions with high Fe content.

AXJ530 is a creep-resistant magnesium alloy patented by GM, with a nominal composition of Mg–5 wt% Al–3 wt% Ca 0.15 wt% Sr [31]. The AXJ530 magnesium alloy has promising mechanical properties, castability, and creep resistance and may have various applications in the automotive industry [32,33]. Although the allowable Fe impurity level is specified to be 40 weight ppm [31], no reason has been given for the impurity tolerance limit in this alloy. There are only very limited studies on the corrosion resistance of AXJ530 alloy [34–37]. Moreover, the mechanism for the influence of iron impurities on its corrosion performance has not been systematically investigated and is not yet well understood.

For a wider application of magnesium alloys, it is important to understand the mechanism of the tolerance limit of impurity. In this paper, several AXJ530 magnesium alloy samples were die cast and a series of phase diagrams were calculated. By comparing the experimental results and the theoretic calculations, the relationship between the Fe impurity level and corrosion performance was studied and the mechanism for the tolerance limit of the Fe impurity in this alloy was discussed.

2. Experimental

2.1. Materials and casting

The commercial magnesium alloy AM50 (Mg–5 wt% Al–0.4 wt% Mn) was used as the base alloy. The primary AXJ530 magnesium alloy ingot, designated as Mg–5 wt% Al–3 wt% Ca–0.15 wt% Sr was prepared in a steel crucible by adding pure calcium (99 wt% purity) and pure strontium (99 wt% purity) to the AM50 magnesium alloy melt, which was gravity cast in a steel die and air cooled. The chemical composition of the primary AXJ530 magnesium alloy ingot for this study is listed in Table 1.

Alloying was performed in a 150 kg capacity induction furnace in which the melt was stirred during the whole process to make sure it was chemically uniform. Before each series of casting, about 100 kg of primary AXJ530 magnesium alloy ingot was heated to 750 °C, at which temperature the desired quantities of the iron impurity and manganese were added in the forms of Al–5 wt% Fe ingot and anhydrous manganese chloride powder, respectively, in order to achieve a melting composition: 5 wt% aluminum, 3 wt% calcium, 0.15 wt% strontium, 0.2 wt%, 0.4 wt% or 0.8 wt% manganese and approximately 350–400 weight ppm iron. It has been discovered that when manganese chloride is added to molten magnesium alloy, it is instantaneously reduced to metallic manganese, accompanied by the formation of magnesium chloride [38,39]. In fact, the addition of anhydrous $MnCl_2$ powder has become standard foundry practice for making magnesium alloy [40], and this method has been successfully used in Dow chemical [11,18–21,41]. It is expected that magnesium chlorides stays in the slag after alloying. Four different casting temperatures (i.e. temperatures of the melted alloy in crucible right before casting) were chosen: 730 °C, 710 °C, 680 °C and 650 °C. Once the desired temperatures were reached and maintained for 10–15 min for stabilization, the melting was fed into a 280 ton magnesium cold chamber die cast machine and cast into a small steel die. Three series of tensile specimens (15 mm in diameter and 185 mm in length) were obtained from this die. The casting parameters for each trial, including casting temperature and die temperature, are listed in Table 2. In trial # X–Y, X represents desired Mn content level (1 represents 0.2 wt% of Mn, 2 represents 0.4 wt% of Mn and 3 represents 0.8 wt% of Mn); Y represents the casting trial in each desired Mn content level, where casting temperature and die temperature may change. The die was pre-heated at 300 °C before casting. However, for some trials, 200 °C was also used to study the effect of die temperature on the corrosion performance of casting magnesium alloy. Therefore the number of the "1#" samples was more than that of the "2#" and "3#" samples.

2.2. Chemical composition analysis

After the casting experiment, a section of a selected tensile bar was analyzed from each casting group to determine its chemical composition. ICP/AES (Inductively-Coupled Plasma/Atomic Emis-