



# Localized Corrosion of Magnesium Alloys in NaCl Solutions Explored by Scanning Electrochemical Microscopy in Feedback Mode



Wenjuan Liu<sup>a,b</sup>, Fahe Cao<sup>a,\*</sup>, Yan Xia<sup>a</sup>, Linrong Chang<sup>a</sup>, Jianqing Zhang<sup>a</sup>

<sup>a</sup> Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China

<sup>b</sup> College of Materials Science and Engineering, Nanjing University of Technology, Nanjing 210009, PR China

## ARTICLE INFO

### Article history:

Received 11 January 2014

Received in revised form 4 April 2014

Accepted 7 April 2014

Available online 15 April 2014

### Keyword:

SECM

Magnesium alloy

Surface film

Chloride ion

## ABSTRACT

Corrosion of magnesium is initiated from film-free region where the pit corrosion is the main corrosion form. The incubation and growth of active spots in film-free region is affected by the concentration of  $\text{Cl}^-$  and the composition of surface film. Application of scanning electrochemical microscopy (SECM) in feedback mode for corrosion study of AM60 and AMCe1 (AM60 with additional Ce) magnesium alloy in different NaCl solutions is presented. SECM mapping mode was also used to monitor the electrochemical processes on AM60 and AMCe1 alloys immersed in NaCl solutions. The results indicate that the electrochemical behavior of magnesium alloy is different depending on chloride ion concentration and its surface film. Enhanced localized corrosion of magnesium alloy with chloride ions concentration shows that higher concentrated chloride ions results in the rapid initiation and quick growth of active spots, facilitates breakdown and high hydration of surface film. Meanwhile, scratch tests were performed on magnesium alloy, known to develop an artificial defect to monitor variation of electrochemical activity. In the proximity of the local defect, the accelerated electrochemistry activity originating from the high-hydration of surface film is observed when chloride ions are concentrated in the environment. Furthermore, the addition of rare earth element Ce is advantage of reducing the tendency of incubation and growth of active spots due to its more complete and protective surface film.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Metallic materials often go through electrochemical corrosion when contacting with the aggressive agents present in the environment. As one of the promising structural materials in aerospace and automotive industry, magnesium alloys also encounter great corrosion damage in their service environment [1–3]. To date, the majority of the current knowledge of corrosion of magnesium and its alloys have been gained from the use of conventional electrochemical methods, such as potential curves, cyclic voltammetry and electrochemical impedance spectroscopy, reflecting the average electrochemical response for the entire surface [4–6]. It is well known that the corrosion is initiated within the range of nanometers and microns and will be terminated as soon as the absence of corrosive medium. Therefore, a comprehensive understanding of corrosion mechanism requires acquisition of data on those scales

in real time under exactly the same conditions in which metal corrodes.

Recently, numerous attempts have been made on magnesium alloys and magnesium-based materials using local probe techniques with enhanced spatial resolution, giving microscopic information on the processes occurring locally at electrochemical active surface. For instance, an in situ scanning vibrating electrode technique (SVET) was introduced to map changes in local electrochemical activity in unpolarized CP magnesium samples freely corroding in NaCl(aq) electrolyte [7]. Moreover, combination of scanning ion-selective electrode technique (SIET) and SVET has been successfully applied in coated magnesium alloy [8–10]. Herein, the pH- and  $\text{Mg}^{2+}$ -selective microelectrodes (pH-SME and  $\text{Mg}^{2+}$ -SME) were prepared to monitor their local spatial distribution on coated magnesium alloy. Among the later, scanning electrochemical microscopy (SECM) is also ideally suited for investigating corrosion processes, providing in situ topographic and electrochemical reactivity information with respect to surface evolution at the micron and sub-micron scale in aqueous solution [11].

As early as 1990s, SECM has been applied for studying pitting corrosion of titanium [12–14], revealing different responses of tip

\* Corresponding author. Department of Chemistry, Zhejiang University, Hangzhou 310027, P.R China, Tel.: +86 571 87952318; fax: +86 571 87951895.

E-mail address: [nelson.cao@zju.edu.cn](mailto:nelson.cao@zju.edu.cn) (F.H. Cao).

current in active and passive regions. So far, SECM has been broadly used to study the electrochemical reactivity and corrosion behavior of metals such as iron [15,16], steel [17–19], zinc [20], aluminum and its alloy [21,22], and titanium [12–14,23,24]. For metals like iron, steel, aluminum and titanium, the cations  $M^{n+}$  or  $O_2$  can be monitored either in feedback mode or generation-collection mode of SECM, such as cations  $Fe^{2+}$ . In the other way, the mercury sphere-cap microelectrode tip was used for the effective amperometric operation of SECM in the detection of metal dissolution during zinc corrosion [20]. However, unlike other metals, for the detection of distribution concentration in magnesium corroding samples with sufficiently negative redox potentials in aqueous solutions, the direct detection of anodic product  $Mg^{2+}$  with Pt microelectrode is impossible to conduct in amperometric mode. On the other hand, the cathodic reaction on magnesium corroding samples is reduction of  $H_2O$  to produce  $H_2$  and  $OH^-$ . Neither of them could be detected using Pt microelectrode in amperometric mode in aqueous solution. Therefore, several SECM researches on magnesium are related to operation of potentiometric mode with ISE (ion selective electrode) to monitor distribution of  $Mg^{2+}$  and pH or indirect illustration about influence of an Mg-rich primer on aluminum alloy with monitoring changes of electrochemical activity on aluminum alloy after coupled with Mg-rich primer coated substrates using  $O_2$  as mediator [25–28]. Meanwhile, SECM experiments were performed using electrolyte resistance between the tip and the substrate as an electrochemical sensor to visualize cracks and holes above the Mg surface after immersion in 0.5 M  $Na_2SO_4$  solution [29]. Despite some promising results, SECM operation in potentiometric mode involves the fabrication of robust ISEs. Its practical application on the investigation of magnesium degradation was still severely limited by the slow response times of the liquid contact micropipette electrodes employed [25]. Herein, investigations on magnesium substrates with SECM in amperometric mode using commercial Pt microelectrode become another pathway to get information on their corrosion behavior in the view of microscopic range [30,31]. Visualization of active regions in the surface was successfully accomplished with detection on changes of added redox mediator in feedback mode rather than directly monitoring  $Mg^{2+}$  in generation-collection mode in the research of Liu [30].

It is proposed that the corrosion of magnesium and its alloys is initiated from film-free region [32–34]. The presence of aggressive aqueous species causes rapid breakdown of the partially protective surface film formed under aqueous conditions and results in higher corrosion rates. Concerns arise particularly from chloride ions since they are widely used as salt for the road, in human nutrition, in the chemical industry and because of their presence in marine environments. Therefore, it is essential to explore the initiation, incubation and growth of active spots in film-free region in NaCl solutions and to investigate the influence of composition of surface film on the pitting corrosion of magnesium alloy for further understanding magnesium corrosion mechanism in aqueous solutions. Since localized corrosion of magnesium, commonly described as pitting, occurred within the range of microns and nanometers, a comprehensive understanding of the corrosion mechanism requires the synthesis of data in those scales. Therefore, SECM is suitable for the observation of changes on electrochemical active surface. Eventually, it is promising to provide a new route to elucidate certain characteristics of magnesium corrosion.

In the present work, SECM operation of amperometric mode was used to explore the initiation, incubation and growth of active points in film-free region and to investigate the influence of composition of surface film on the pitting corrosion of magnesium alloy in NaCl solutions. The aim of these non-perturbing, *in situ* studies is to characterize any observed localized corrosion phenomena by

time-resolved, local current distribution above a corroding magnesium surface.

## 2. Experimental

AM60 specimens were cut from an as-cast ingot which was obtained from Jiaying Asia Magnesium Technology Co. Ltd., Chinese Academy of Sciences. The chemical composition (wt%) detected with direct-reading spectrometer SPECTROMAXx made by SPECTRO Analytical Instruments GmbH & Co. KG, is presented as follows: 5.79 Al, 0.13 Zn, 0.316 Mn, 0.023 Si, <0.0012 Fe, 0.0019 Cu, <0.0015 Ni, 0.0009 Be and balance Mg. Magnesium alloy containing 0.82 wt% cerium (AMCe1), which resembles AM60 alloy in chemical composition except cerium content, with optimum corrosion resistance in NaCl solutions was chosen based on our previous study [35]. Magnesium alloy column, with the cross section 6.0 mm in diameter, was embedded in polytetrafluoroethylene (PTFE) so that only a single flat surface was exposed to solution. Prior to each test, samples were dry grounded through successive grades of silicon carbide abrasive papers from 400# to 1000# followed by alumina finishing to 0.3  $\mu m$  in water, degreased with acetone, washed with deionized water and dried in cool flowing air.

SECM tests were performed using a commercial SECM system CHI 920C (CH Instrument) consisting of a motor control and a bipotentiostat. All the measurements were operated in a three-electrode configuration utilizing a Pt probe 10  $\mu m$  in diameter as the working electrode, a Ag/AgCl/KCl (3 M) reference electrode and a platinum wire as a counter electrode, leaving magnesium specimens unbiased during experiments at their corresponding open circuit potential. All tip potential cited here is referred to the Ag/AgCl/3 M KCl reference electrode. The potential of Ag/AgCl/3 M KCl reference electrode is 0.194 vs SHE (standard hydrogen electrode)/V according to Nernst equation at 25 °C.

Ferrocene-methanol (FcMeOH) (Alfa Aesar China Co., Ltd) of 1.0 mM concentration was added into NaCl solutions (Aladdin chemistry Co., Ltd) as redox mediator in feedback mode. All solutions were prepared from spectrographic grade chemicals and Millipore-Q water (18.2 M $\Omega$  cm). The tip was biased at +0.5 vs (Ag/AgCl/3 M KCl)/V to ensure complete diffusion-limited oxidation of ferrocene to ferrocinium [36]. The operating distance of the microelectrode tip over the surface was respectively set at 5, 8 and 10  $\mu m$  by measuring approach curves and fitting them according to expressions of Cornut [37]. Images were required by tip raster scanning 200  $\mu m \times 200 \mu m$  over magnesium surface with scan rate 40  $\mu m s^{-1}$  (1  $\mu m/0.025 s$ ). During SECM experiments, we introduced scratches into our samples by deliberately mechanical damage with a conically-shaped tip of 30  $\mu m$  radius. The tip was vertically pressed on the magnesium alloy and imposed a general force by hand. Then, the scratch was observed by Stereo Microscopes (JSZ6S, Nanjing Jiangnan Novel Optics Co., Ltd.) to make sure that an obvious and relatively deeper scratch was introduced, aiming at easily positioning its location in NaCl solutions and preventing the difficulty to distinguish the scratch without brilliance after several minutes taking for approach curves measurements. Line scan was obtained over a scratch in the direction of X for the length of 700  $\mu m$  with 0.1  $\mu m$  steps at 20 ms, resulting in test time of approximately 160 s per scan. Ex-situ characterization of scratch and corrosion surface after SECM tests was performed with Hitachi TM3000 scanning electron microscopy (SEM) with operation energy of 15 kV. The measurement of surface roughness ( $R_a$ ) and the depth and width of scratches were conducted with Veeco Dektak 150 surface profilometer. The parameters are followed. Scan rate was set 500  $\mu m$  (scan length)/60 s (scan duration) in standard scan mode with the scan resolution 0.028  $\mu m/sample$ . At least three parallel measurements were acquired on each scratch.

Download English Version:

<https://daneshyari.com/en/article/185789>

Download Persian Version:

<https://daneshyari.com/article/185789>

[Daneshyari.com](https://daneshyari.com)