Electrochimica Acta 227 (2017) 136–151

Contents lists available at ScienceDirect

Electrochimica Acta

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

Effect of Crystallographic Orientation on the Corrosion of Magnesium: Comparison of Film Forming and Bare Crystal Facets using Electrochemical Impedance and Raman Spectroscopy

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ARTICLE INFO

Article history:
Received 9 September 2016
Received in revised form 15 December 2016
Accepted 18 December 2016
Available online 21 December 2016

Keywords:
crystallography
magnesium
electrochemical impedance spectroscopy
surface energy
electron backscatter diffraction

ABSTRACT

The corrosion rate of Mg indicates a strong crystallographic dependence in chloride-containing, alkaline environments that correlates inversely with oxide film thickness. In contrast, a different crystallographic orientation dependency is observed initially during open circuit corrosion in non-chloride containing, near neutral pH buffered, chelating environments such as Tris(hydroxymethyl)aminomethane (TRIS) and Ethylenediaminetetraacetic (EDTA) which minimize air-formed MgO oxides. The origins of the differences in the rates of the coupled corrosion processes as a function of crystallographic orientation were investigated utilizing electrochemical impedance spectroscopy (EIS) and Raman vibrational spectroscopy. High frequency constant phase elements (CPEs) were exploited to determine oxide thicknesses as a function of crystal orientation. In unbuffered NaCl, open circuit corrosion was faster on basal planes while lower corrosion rates were observed on low index, prismatic and pyramidal planes. This variation in rate with crystallographic orientation in 0.6 M NaCl was interpreted to depend on the MgO and $Mg(OH)_2$ film thicknesses as a function of orientation. In particular, crystal planes with a lower $MgO/Mg(OH)_2$ thickness corroded at higher rates as assessed in-situ by EIS and suggested by Raman spectroscopy. The crystallographic orientation dependence of corrosion seen initially upon exposure in the buffered neutral pH environments corresponded with crystal facet surface energy for bare Mg but this trend disappeared with exposure time and $Mg(OH)_2$ films were then detected.

1. INTRODUCTION

1.1. Corrosion Dependence on Crystallographic Orientation for Various Metal Systems

For many metals and alloys, the corrosion rate has been found to exhibit strong dependence on crystallographic orientation [1–5]. Assessing anisotropic corrosion properties by using single crystal samples limits the number of facets tested [3,4,6,7]. While such studies give an indication of the corrosion properties of specific orientations, limitation to a few crystal planes can confound understanding of the corrosion properties of the system as a whole [3,4,6,7]. This paucity of grain orientations at closely spaced h, k, l Miller-Bravais indices values falls short because corrosion properties can vary significantly over only a few degrees difference in crystallographic orientation [1]. Consideration of a large number of grains on polycrystalline samples on a grain by grain basis over small differences in h, k, l values provides the opportunity to uncover the true orientation dependence of dissolution and corrosion rate as a function of surface plane orientation.

Moreover, significant differences in findings as well as interpretation of crystal orientation effects on corrosion often occur [1–13]. For body-centered cubic (bcc) stainless steel in 0.6 M NaCl, the highest percentage of pitting events was observed on planes oriented $\sim 25^\circ$ away from {001} [8] while in contrast the {100} orientation was reported to have the highest corrosion rate in H_2SO_4 [2] and NO_3^- [9]. For face-centered cubic (fcc) Al in NaOH, orientations near {111} indicated the most corrosion [10–12]. The effects of crystal structure on atomic bonding between nearest neighbors, coordination, the number of dangling bonds and

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http://dx.doi.org/10.1016/j.electacta.2016.12.107
0013-4686/

resultant surface energy, film thickness, film/substrate epitaxy [1,2,6,13] as well as the reaction thermodynamics and kinetics at the metal-oxide-solution interface during both passive and active corrosion should all be considered to better understand the influence of crystallographic orientation on corrosion [3,7]. However, a careful comparison is required on the same alloy under both film covered and bare, actively dissolving conditions because orientation effects may differ in each case.

1.2. Crystallographic Orientation Dependence on Corrosion for Mg and Mg Alloys

A systematic sampling of orientations in Mg alloys is lacking or has been complicated due to the substantial crystallographic texture of Mg alloy sheet or plate often formed upon mechanical processing [14–17]. For these reasons, as well as the historical inability to accurately assess corrosion and dissolution rates in Mg system by electrochemical methods [18–20], conflicting results have been reported regarding the orientation dependence of Mg corrosion [21,22]. Corrosion was observed on planes that were oriented with a normal near the $\langle 0001 \rangle$ direction with respect to the sample surface in NaCl environments containing dichromate ions [23]. One study examined Mg in 0.1 N HCl and studied grains after EBSD and AFM where the (0001) planes were argued to be most corrosion resistant [22]. The basis for this claim is unclear. Many grains with high orientations exhibited striations after corrosion that were argued to be made up of $\{20\bar{2}1\}$, $\{0001\}$, $\{11\bar{2}0\}$ and $\{01\bar{1}0\}$ planes. Some of these facets are likely slowly dissolved planes seen after fast dissolving planes grow themselves out of existence as shown elsewhere [1]. When tested in NaCl, the rolling plane (heavily textured to favor the basal plane) of wrought AZ31 exhibited greater H_2 evolution than cross-sections suggesting an effect of texture on corrosion rate but the difference was later attributed to the prevalence of particles such as Al_8Mn_5 and not crystal orientation effects [21,24]. The Mg (0001) surface exhibited pitting corrosion susceptibility at the open circuit potential (OCP) while the $(10\bar{1}0)$, and $(11\bar{2}0)$ surfaces were passive at open circuit and pitting only initiated at potentials slightly anodic to their open circuit potentials in a similar environment [25].

Validation of the corrosion rate of various crystallographic orientations in Mg based materials has also involved alloys [26,27]. Mg-Al alloys (such as AZ31) corroded at a lower rate on the closely packed basal plane [26], although this was also complicated by the presence of secondary phases. In another study, SKP, SVET, EIS and E-log(j) were focused on two Mg grains in NaCl and saturated $Mg(OH)_2$ solution [21]. One had an orientation between (0001) and $(10\bar{1}0)$ and the other was close to $(11\bar{2}0)$ on a grain facet which also contained twins. The grain near (0001) had the greatest corrosion rate by EIS and E-log(j) and the oxide film was thinner, which is similarly shown by the work in this study. The corrosion dependency might have been governed by film thickness as the (0001) film was thinner. This was not reported but evident from the work. The authors were instead concerned that films "concealed" the effects of orientation, not recognizing that it might be a controlling factor [21]. No other orientations were attempted. Therefore, there is limited comprehensive comparison between the corrosion rate and overall effects of dissolution on the resultant morphology on many individual grains as a function of crystallographic orientation not clouded by these factors.

The work herein comprises of a full analysis of the EIS frequency response on polycrystalline materials as well as an in depth analysis on the corrosion morphology via SEM and Electron Backscatter Diffraction (EBSD). Rate data is correlated with Raman spectroscopy in both attempts to produce film free and film covered cases. In work to date on the crystallographic orientation on Mg, while there has been some work on polycrystalline pure Mg samples [21,22], the work has only evaluated a few orientations and has not shown a wide breath in the evaluation techniques. In particular EBSD correlated with surface topography measurements, such as profilometry techniques now enables understanding of the dissolution behavior of a large number of crystal planes [1] as has been performed here. In this study, these prior difficulties have been overcome by EBSD analysis of many grains. Profilometry and electrochemical impedance spectroscopy (EIS) were both conducted on individual, isolated grains to reveal the orientation dependence of corrosion under open circuit conditions.

1.3. Effect of Surface Energy on Crystallographic Dissolution

Existing literature on Mg suggests that surface energy varies with crystal orientation. The surface energy for Mg $\{0001\}$, $\{10\bar{1}0\}$ and $\{10\bar{1}2\}$ surfaces are 0.9, 1.2 and 1.4 J/m^2, respectively, as calculated with empirical electron theory [6,28]. This implies that exposed faces close to the $\{0001\}$ plane should have a lower thermodynamic driving force and might corrode slower than those planes which are oriented slightly different than the $\{0001\}$ plane from a surface energy minimization perspective [23]. Previous work on bare fcc Fe-Pd shows that the highest dissolution occurred at planes oriented approximately 45° from the $\{100\}$ orientation which correlated to the highest determined surface energy [1]. However, Mg is a system which corrodes in $[Cl^-]$ solutions far from equilibrium [1].

1.4. Nature and Crystallographic Aspects of the Native Oxide Film on Mg

For Mg, the oxide film is affected by factors such as solution pH, where a more protective film is typically formed in alkaline solutions [29–32]. Several techniques have been used to analyze the nature of this film. The surface film formed on Mg is duplex in nature, consisting of a thin, nano-crystalline MgO inner layer and a $Mg(OH)_2$ platelet layer [33–35]. X-ray photoelectron spectroscopy (XPS) [36–38] and focused ion beam (FIB) [29,35,39] studies on the surface of Mg have shown that the surface film consists of both MgO and $Mg(OH)_2$ [40]. The initial, crystalline MgO layer is formed during exposure to air. Hydration of the bulk inner MgO layer occurs and the layer thickens to form the outer $Mg(OH)_2$ corrosion product [29,35]. The thickness of the oxide layer on Mg has been calculated through XPS and FIB cross-section [29,35,39]. While this thickness is extremely dependent on exposure time and environment, the outer, $Mg(OH)_2$ layer is typically on the order of ~500 nm in thickness and flake-like while the inner MgO layer is only on the order of 50–90 nm thick [29,35,39]. MgO films on the basal $\{0001\}$ surface are thinner than those on either $\{01\bar{1}0\}$ and $\{11\bar{2}0\}$ in dilute sodium sulphate solutions [41]. This relationship has been similarly reported for polycrystalline hexagonal close packed (hcp) Ti using EBSD measurements [42]. While the $\{0001\}$ and $\{01\bar{1}0\}$ planes consist of equiaxed crystals of MgO, the $\{11\bar{2}0\}$ surface forms MgO with oriented flakes perpendicular to the metal/oxide interface [29,35].

1.5. Opportunity to Ascertain Crystallographic Dependence of Simultaneous Corrosion and Oxide Formation with Impedance Spectroscopy

The use of electrochemical impedance spectroscopy (EIS) gives a reliable and repeatable estimation of the instantaneous corrosion rate on Mg and its alloys [18–20]. The components of the equivalent circuit have been shown to correspond to the Mg