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In situ AFM studies of the stability of MgO(1 0 0) in aqueous electrolytes

Ignacio Giner *, Ozlem Ozcan, Guido Grundmeier

Department of Technical and Macromolecular Chemistry, University of Paderborn, Warburger Str. 100, 33098 Paderborn, Germany

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ABSTRACT

The stability and dissolution of MgO(1 0 0) single crystal surfaces in alkaline solutions of $NaClO_4$ and NaCl were investigated by means of in situ atomic force microscopy (AFM) and ex situ angle resolved X-ray photoelectron spectroscopy (AR-XPS). MgO surfaces showed higher resistance to dissolution in $NaClO_4$ electrolyte due to the formation of a gel-like hydroxide layer. The emergence of rectangular/square formed pits oriented in the ⟨1 1 0⟩ directions during immersion in NaCl electrolytes at alkaline pH was observed. The results are discussed on the basis of a substitution of hydroxides by chlorides at the electrolyte/MgO interface.

1. Introduction

The resistance of metals and alloys against the attack in corrosive electrolytes or gases is primarily related to the electrical properties and the chemistry of the surface oxide film [1]. In order to optimize the corrosion resistance in a certain metal, it is necessary to have a profound understanding of the properties of the oxide film [2]. A detailed mechanistic explanation of the changes taking place on oxide surfaces in aqueous environments is particularly challenging because of the complexity of the involved processes, which include selective etching, hydration, and the formation of secondary phases. In this context, Mg based alloys develop a protective hydroxide layer in aqueous electrolytes, which reduces the degradation rate at the early stages of corrosion [3,4]. However, the efficiency of the temporary protective hydroxide layer mainly depends on the pH and the presence of corrosive adsorbates. Cl^- is one of the most active adsorbates which causes a massive degradation on Mg based alloys due to its high affinity towards Mg ions [5,6], leading to the deterioration of the passive film [7–9].

Single crystalline MgO(1 0 0) surfaces are often described as a model system for studying the changes on amorphous or polycrystalline magnesium oxides under exposure to corrosive electrolytes [10,11]. Even though it was controversially discussed in the literature, nowadays water dissociation on the defect-free MgO(1 0 0) surface is widely accepted [12–16]. Liu et al. observed that water dissociation initiates at the defect sites and expands to the defect-free terrace sites [15]. In water based solutions at a lower pH than the point of zero charge (PZC) of MgO at pH 12.4, the surface undergoes a reconstruction via hydroxylation [17–19]. At a low coverage of surface hydroxides (<50%), the stability of the interface is mainly determined by a subtle balance between the maintenance of the hydrogen bond network within the water layer and the formation of hydrogen bonds to the oxide ions in the surface layer [20,21]. At a higher coverage of surface hydroxides, the hydrogen bond network cannot stabilize the surface [11,22–26]. Hence, the dissolution of MgO is kinetically controlled by the rate of surface protonation, where the thermodynamically favorable reconstruction mechanism is the formation of (1 1 0) faces [21,23,24]. Prolonged exposure results in the formation of (1 1 1) faces on (1 0 0) oriented cubic MgO structures [18,19].

The formation of a hydroxide phase on the MgO surface has been a topic of controversial discussion. Some authors suggested that the formation of a protective hydroxide phase occurs when the etched Mg^{2+} ions cannot diffuse away from the surface, leading to a re-precipitation on the MgO surface [27]. However, other authors reported that the protonation of the MgO lattice due to water ingression is a more plausible mechanism for the formation of $Mg(OH)_2$ from MgO rather than the precipitation [22,28]. The similar corrosion rates for MgO and $Mg(OH)_2$ at acidic pH support this hypothesis [22].

Localized interaction of Cl^- with oxide surfaces has been widely studied in the literature. In some cases, as in NiO, the chloride ion adsorbs on the passive film, followed by the penetration of Cl^- into the oxide layer, which leads to severe pitting corrosion [29]. However, the basic mechanisms of chloride adsorption on MgO surfaces, i.e. whether it is physisorption or chemisorption and how it depends on coverage, still remained unclear [25,26]. Despite a considerable amount of research on localized corrosion, knowledge on the passivity breakdown and pit initiation at the nanoscopic and

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* Corresponding author. Tel.: +49 5251 605746; fax: +49 5251 603244.
E-mail address: iginer@mail.uni-paderborn.de (I. Giner).

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atomic scale, as well as the reason for its local occurrence, remains limited.

In this work, the role of the chloride anion on the dissolution behavior and the hydroxide phase formation on MgO surfaces are investigated. The dissolution behavior was studied at low coverage of surface hydroxides by using an alkaline pH closer to the point of zero charge of the surface (PZC = 12.4). This approach enabled the in situ investigation of the formation of the hydroxide phase at MgO surfaces and the inhibition of the corrosion processes. Morphological changes of the surface were studied by means of in situ atomic force microscopy (AFM), whereas the hydroxide phase formation, as well as the hydroxylation degree of the surfaces were evaluated by means of angle resolved X-ray photoelectron spectroscopy (AR-XPS).

2. Experimental

2.1. Chemicals and materials

All chemicals and solvents were of p.a. grade (analytical reagent grade) and used without any further purification. Deionized water was obtained from an Ultraclear TWF (SG Wasseraufbereitung, Barsbüttel, Germany) system with a maximum electrical conductance of 0.055 μS cm^{-1}. For cleaning purposes, hydrogen peroxide (35%, Stockmeier Chemie GmbH & Co KG, Germany), and ammonia (25%, Stockmeier Chemie GmbH & Co KG, Germany) were used. The epi-polished single crystals with crystallographic orientation (100) were purchased from MaTeck GmbH (Juelich, Germany), with dimensions of 20 × 20 × 0.5 mm^3 and 10 × 10 × 0.5 mm^3 (length, width and height). The electrolytes used for the experiments were 1 mM $NaClO_4$ (>99%, Merck, Germany) and NaCl (>99%, Merck, Germany) solutions. The pH of the solutions was adjusted to pH 11 adding appropriate amounts of 1 mM NaOH (>99%, Merck, Germany), 1 mM $HClO_4$ (>99%, Merck, Germany) or 1 mM HCl (>99%, Merck, Germany) solutions, to sustain a constant ionic strength.

2.2. Sample preparation

MgO single crystals with (100) orientation were processed according to the procedure proposed by Aswal and Bennedetti in order to obtain atomically flat surfaces [30,31]. Briefly, the as-received crystals were annealed in air at 1250 °C for 12–18 h.

2.3. Atomic force microscopy

AFM measurements in air and liquid were performed with a JPK Nanowizard II Ultra (JPK Instruments AG, Berlin, Germany) equipped with an anti-noise- and anti-vibration-box. A commercial in situ measurement cell was used for imaging the single crystals during exposure to corrosive electrolytes. The liquid cell was purged with the electrolyte enabling an exchange of the electrolyte every 3 min. All AFM images were recorded in intermittent contact mode. The scan speed was 1 μm per second, at a scan resolution of 512 × 512 pixels. Rectangular silicon cantilevers type NSC19 (Mikromesh, Estonia), with a resonance frequency of about 80 kHz in air and a force constant of 0.1–0.3 N m^{-1} were used.

During in situ AFM imaging tip wearing and tip induced effects have to be minimized in order to assess the quality of the images obtained. Suarez et al. performed longer in situ contact mode AFM measurements on MgO(100) surfaces at acidic pH observing an increased deterioration at the scanned area when compared to the areas outside the scan window [23]. In our studies, intermittent contact mode measurements were performed to minimize tip wear, and different areas were scanned during the in situ measurements in order to evaluate any tip induced effects. The electrolyte pH was measured during the in situ measurement to assess the quality and reliability of the measurements. Furthermore, ex situ AFM measurements were performed at different exposure times confirming the features observed during in situ scanning. For the ex situ AFM measurements, the MgO(100) surfaces were immersed in the corresponding electrolytes for the selected time. Then, the samples were rinsed with milli Q water and dried with nitrogen.

2.4. X-ray photoelectron spectroscopy

XPS measurements were performed by means of an Omicron ESCA + system (Omicron NanoTechnology GmbH, Germany) operated at a base pressure of $<5 \times 10^{-10}$ mbar. The system is equipped with a hemispherical energy analyzer and the element spectra were recorded at a pass energy of 25 eV. For photoelectron excitation a monochromated Al Kα (1486.7 eV) X-ray source with a spot diameter of 600 μm was used. The take-off angle of the detected photoelectrons was 20–70° with respect to the surface plane. The calibration of the spectra was performed using the C 1s peak (binding energy BE = 285 eV) as an internal reference. For data evaluation, the Casa-XPS software was used [32]. The quantification of the XPS data was performed by integration of the peaks taking into account the relative sensitivity factors of the elements.

2.5. Low enery electron diffraction

Low energy electron diffraction (LEED) experiments were performed by means of an Omicron Spectra LEED system (Omicron NanoTechnology GmbH, Germany) at an incident angle of the electron beam close to 90° with respect to the surface plane. The beam energy was adjusted between 80 eV an 250 eV to yield optimum LEED patterns.

3. Results

3.1. Characterization of the MgO(100) surface

Fig. 1a shows an AFM image of a MgO(100) surface after high temperature annealing, which resulted in the formation of atomically smooth 500–1000 nm wide terraces (Fig. 1b), separated by steps of heights ranging between 0.4 nm to several nanometers (Fig. 1a).

The lowest step height observed in this study was 0.42 nm, which corresponds to the unit cell height of the MgO lattice [21]. The dissimilar step heights can be explained by the step bunching effect [27]. At high annealing temperatures, the reconstruction of the steps on the surface becomes kinetically unstable leading to the existence of high step bunches [30].

The LEED pattern of the MgO(100) crystal obtained at an energy beam of 90 eV is presented in Fig. 1c. A typical rock-salt structure is clearly observed [30,33]. The LEED pattern presents a diffuse background which could result from adsorbed contaminations from the ambient laboratory atmosphere [34].

Fig. 2 shows an XPS survey spectrum measured at an angle of 70° with respect the surface which contains signals of magnesium, oxygen and some residual surface carbon, originating from atmospheric contaminations. Considering the 70° measurement angle leading to an information depth of ~2.5 nm, the level of surface carbon species was determined to 10.5%.

Fig. 3 shows the AR-XPS data for the O1s, C1s and Mg2p elemental spectra at 70° and 20° take off angle. The O1 core level confirms the presence of hydroxides, adsorbed water and carboxyl groups located on the oxide surface. The O^{2-} contribution, the OH^- contribution and the contributions of adsorbed water and