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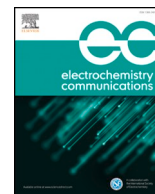
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Mechanism of hydrogen formation during the corrosion of Mg₁₇Al₁₂

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ABSTRACT

Previous investigations (DFT calculations) showed that hydrogen atoms adsorption and H₂ desorption can occur on MgO and Al₂O₃ and that H atoms can diffuse on Mg and Al surfaces. However, these three simultaneous actions, *i.e.* H adsorption, H diffusion and H₂ desorption, have not been experimentally proved. In this paper, we propose a mechanism of formation of H₂ during the corrosion of an intermetallic compound Mg₁₇Al₁₂ in 3.5 wt. % NaCl aqueous solution based on *in situ* Raman spectroscopy analysis. We found that, through the passivation zone (*e.g.* *E* varying from the open circuit potential (OCP) to +100 mV/OCP), the oxide layer is destroyed in favor of the appearance of Mg and H atoms. Moreover, the formed H atoms are adsorbed on the oxide surface and then diffuse on either the oxide surface or the unreacted metal surface where they recombine forming H₂. *In situ* Raman measurements during anodic polarization experimentally prove, for the first time, the formation of a reaction intermediate which weakens the H–H bond. The obtained results explain the mechanism of hydrogen production under anodic polarization of the intermetallic compound at normal conditions of temperature and pressure.

1. Introduction

The spillover effect is generally defined as the transport of an active species (*e.g.* H₂) adsorbed or formed on a surface to another surface that does not adsorb or form the active species under the same conditions [1]. Reverse spillover of hydrogen is explained as the migration of adsorbed H atoms from a receptor to a source, where they recombine and desorb as H₂ molecules [2]. The interaction of a hydrogen atom/hydrogen molecule and of hydrogen containing molecules with MgO [3–11] and Al₂O₃ [12,13] has been studied both experimentally and theoretically. The evidence of heterolytic splitting of H₂ was reported a long time ago by experiments performed on MgO powders [5,10] and by *ab initio* calculations [9,11,14,15]. An unpaired hydrogen (*i.e.* H atom) can diffuse on O-sites of MgO above the surface with lower activation energy than that of paired hydrogens, where the diffusion distorts the surface [16]. The interaction between a hydrogen atom and the surface of MgO is weak as the binding energy of a hydrogen atom is small for MgO and the change in free enthalpy is strongly positive when H atoms migrate to the surface of a nonreducible support [3]. H₂ molecules dissociate at (100) MgO surface defects [17], because defects have a radical character and can thus bond (radical) H atoms [18]. The reconstructed MgO (111) surface exposes neighboring low-

coordination Mg²⁺ and O²⁻ ions that bond hydrogen to form OH⁻ and MgH⁺ [19]. Similarly, hydrogen atoms adsorb dissociatively on aluminum and its oxide with the formation of Al–H [20] and H⁻ [13] respectively. Additionally, the diffusion of atomic H on the Mg surface and Al surface is energetically favorable [20,21].

Magnesium alloys are promising lightweight materials for aerospace, automobile, consumer electronics and biodegradable implants due to their low density and high specific strength [22–25]. Mg–Al alloys are the most common category of magnesium alloys where Mg can form with Al an intermetallic compound Mg₁₇Al₁₂. Nevertheless, magnesium alloys are reactive in marine environments [26–28]. The corrosion behavior of pure Mg₁₇Al₁₂ has been reported previously [29,30]. The hydrogen produced during the corrosion of Mg-based materials can be used as an energy carrier for clean energy economy.

Here, we report the examination of the surface modification by collecting vibrational Raman spectra during anodic polarization of Mg₁₇Al₁₂ in 3.5 wt.% NaCl solution. Increasing the potential beyond the OCP led us to observe the hydrogen formation, by the cathodic reaction (*i.e.* reduction of water), and its possible adsorption on the formed MgO and Al₂O₃ during the corrosion of Mg₁₇Al₁₂. Diffusion of H atoms from the oxide to the metal surface is verified experimentally by the integration of peaks from the corroded surface in the Raman spectra.

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2. Material and methods

Before corrosion tests, the as-cast $Mg_{17}Al_{12}$ (Extended Data Fig. 1) was mechanically polished up to 4000 grit SiC paper with absolute ethanol as lubricant until a clean surface was obtained. A conventional three-electrode configuration was used with $Mg_{17}Al_{12}$ as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a titanium grid as the counter electrode in a model seawater solution (i.e. 3.5 wt.% NaCl aqueous solution) to perform the “electrochemical measurement” using a Biologic SP-150 potentiostat with a current resolution of 760 pA and a voltage resolution of 5 μ V. For the anodic polarization test, the sample was maintained for 60 min at OCP in the model seawater solution until it reaches its steady-state as previously observed [29], then, the potential was switched to -50 mV/OCP and scanned up to 100 mV/OCP at 0.05 mV/s. Therefore, $Mg_{17}Al_{12}$ was immersed in the solution for 110 min: 60 min for the OCP measurement and 50 min for the anodic polarization test. During the anodic polarization (from -50 mV/OCP to $+100$ mV/OCP at 0.05 mV/s), vibrational Raman spectra were recorded with a Labram HR Evolution Spectrometer (Horiba Jobin Yvon, Villeneuve d’Ascq, France) using a 532 nm wavelength laser as the excitation source. An Olympus LUM-PlanFl 100 \times /1.00 water immersion objective allows the incident laser beam to be focused on a micrometer-sized part of the sample (Extended Data Fig. 2a and b). Raman spectra were collected in the 400–4380 cm^{-1} range near a corroded area (Extended Data Fig. 2c). Reference spectra acquired by measuring the Raman spectra of the salt solution (e.g. 3.5 wt.% NaCl), Mg, Al (pure Al (fcc crystal structure) do not show Raman spectra in similarity to zirconium metal (bcc crystal structure) [31] so that the peaks observed in Extended Data Fig. 3c are attributed to the thin oxide layer covering Al particles), MgO and Mg(OH)₂ were taken as reference (Extended Data Fig. 3). The corroded surface of $Mg_{17}Al_{12}$ after anodic polarization was analyzed using a TESCAN VEGA3 SB scanning electron microscope equipped with an energy dispersive X-ray spectrometer for the identification of magnesium, aluminum and oxygen.

3. Results and discussion

3.1. Surface modification during anodic polarization

Fig. 1a shows the evolution of peaks in the Raman spectra for different duration of the polarization test (where 60 min is the start of the polarization test).

Peaks attributed to pure Mg crystalline modes (between 960 cm^{-1}

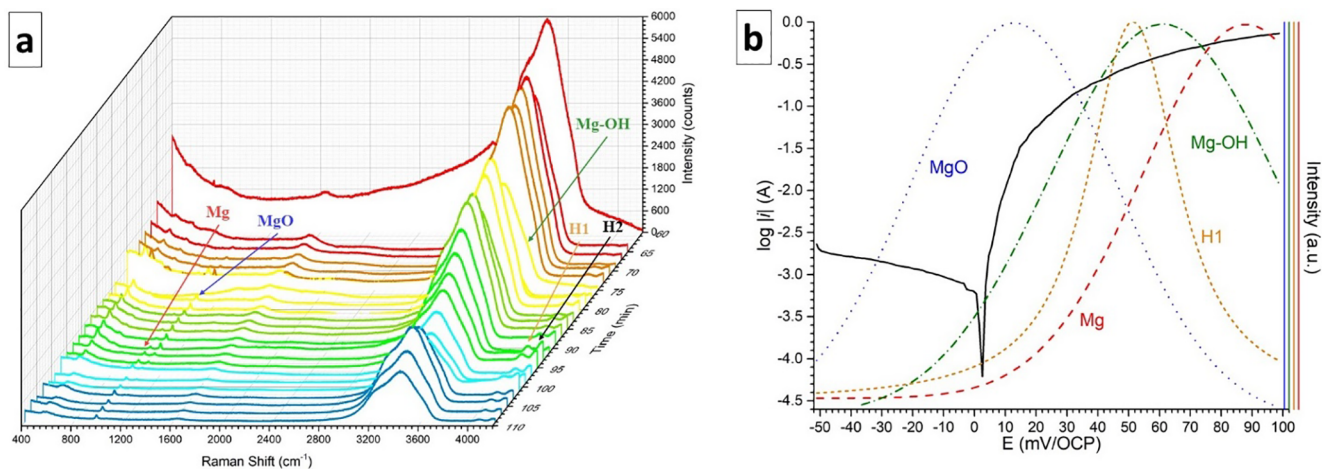


Fig. 1. a) Vibrational Raman spectra of $Mg_{17}Al_{12}$ under anodic polarization as a function of time and b) anodic polarization plot of $Mg_{17}Al_{12}$ from -50 mV/OCP to $+100$ mV/OCP and the corresponding variation of the intensities of the Mg peak (960–1000 cm^{-1}), MgO peak (1030–1110 cm^{-1}), Mg-OH peak (3650 cm^{-1}), and H1 peak (4015–4135 cm^{-1}).

and 1000 cm^{-1}), Mg–O vibration (between 1030 cm^{-1} and 1170 cm^{-1}), Mg–OH vibration (between 3600 cm^{-1} and 3700 cm^{-1}) were observed as well as other peaks during the anodic polarization of $Mg_{17}Al_{12}$. The peaks shown in the 400–2000 cm^{-1} (Extended Data Fig. 4a) are identified as follows: 500–630 cm^{-1} is characteristic of Mg materials (in pure Mg, $Mg_{17}Al_{12}$ or MgO), 630–720 cm^{-1} to NaCl, MgO and $Mg_{17}Al_{12}$, between 960 cm^{-1} and 1000 cm^{-1} to pure Mg crystalline modes, between 1030 cm^{-1} and 1170 cm^{-1} to MgO, the broad peaks in the 1230–1500 cm^{-1} and 1500–1720 cm^{-1} range may be respectively (i) an overlap of the fluorescence of Mg(OH)₂ and the OH bending of water and (ii) Al₂O₃ present on the surface of Al. Furthermore, the broad peak in the 3000–3770 cm^{-1} range (Extended Data Fig. 4b) consists of three overlapped peaks: those of the OH stretching modes centered at 3233 cm^{-1} and 3393 cm^{-1} and the third peak at 3650 cm^{-1} is attributed to Mg-OH vibration (Extended Data Fig. 3d and e). The two peaks (denoted H1 and H2 respectively) shown in the 4015–4135 cm^{-1} range and 4135–4255 cm^{-1} range are not, we believe, identified as H₂; the vibration of dissolved H₂ in water is located at 4138 cm^{-1} [32]. Meanwhile H1 and H2 are observed in the vibrational region of molecular hydrogen. These two peaks could be attributed to the molecular hydrogen formed at the interface solid/electrolyte. The broad H2 peak is characteristic of highly bonded molecular hydrogen interacting with its environment, and exhibits a frequency slightly higher than that of dissolved H₂ in water. The low vibration frequency of H1 indicates a weaker intramolecular interaction compared to the standard H–H interaction. This weaker interaction may be a result of reinforced interactions between the formed hydrogen and its environment. On one hand, Song *et al.* [33] considered that monovalent magnesium ion (Mg⁺) is formed during the corrosion of magnesium. On the other hand, the formation of MgH⁺ [19] in MgO was reported previously. These species may weaken the H–H bond, favoring the appearance of a shifted Raman peak H1. Even though Ma *et al.* [34] provided an estimation of the free energy of formation of Mg⁺ implying that it may be the expected surface species, this hypothesis cannot be adopted without evaluating the effect of Mg⁺ on the vibration frequency of the H–H bond.

Fig. 1b shows the variation of the peaks attributed to Mg, MgO, Mg(OH)₂ and H1 as a function of the applied potential. Applying a higher potential than the OCP leads to the destruction of the passivation layer (MgO), localized by pitting corrosion induced by Cl⁻ ions [35], favoring the appearance of fresh Mg and Mg-OH. Furthermore, the intensity of H1 peak increases simultaneously with both the Mg and Mg-OH peaks. The proposed mechanism of H₂ generation after the breaking of the passivation layer is illustrated in Fig. 2.

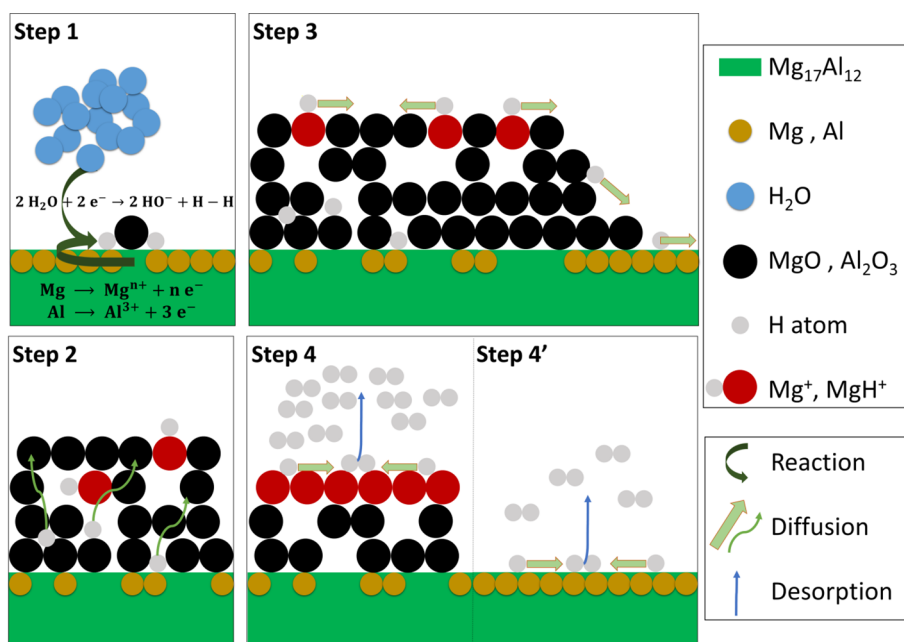


Fig. 2. Scheme of hydrogen production during $\text{Mg}_{17}\text{Al}_{12}$ anodic polarization considering the generation, the adsorption and the diffusion of H atoms as well as H_2 desorption.

The author's previous work shows that the reaction of $\text{Mg}_{17}\text{Al}_{12}$ in HCl produced $\text{Mg}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ and unreacted Al [36]. Reaction of $\text{Mg}_{17}\text{Al}_{12}$ with water generates H atoms by the reduction of H_2O (step 1) and forms MgO and Al_2O_3 on the surface (Extended Data Fig. 5). The formed H atom diffuses through the metal oxide film and is adsorbed on MgO and Al_2O_3 to form MgH^+ [19] or to interact with H_2 (step 2). Since the diffusion of H on Mg and Al is favorable [18,19] (step 3), two H atoms recombine either on the MgO - Al_2O_3 surface (step 4) or the unreacted $\text{Mg}_{17}\text{Al}_{12}$ surface (step 4') to form an H_2 molecule and desorb. However, since the H-atoms are formed during the corrosion of Mg, step 4 is more favorable than step 4'.

3.2. Corroded zone mapping

Raman mapping of the corroded surface after the anodic polarization test (Fig. 3 and Extended Data Fig. 6) revealed the presence of more peaks than those shown in Fig. 1.

After the reaction of $\text{Mg}_{17}\text{Al}_{12}$ with salt water, the corroded surface is covered by Mg and MgO (Fig. 3b, c and d), while energy dispersive X-ray (EDX) mapping (Extended Data Fig. 5) revealed the presence of two zones: the corroded surface (consisting of Mg-Al-O) and the non-corroded surface (consisting of Mg-Al). H1 and H2 enrichment is found on the oxide surface (Fig. 3e and f) proving the adsorption of H atoms on MgO and Al_2O_3 , while the intensity of H1 decreases in the direction of the Mg-Al surface. The formation of the hydrogen atoms is dependent on the formation of the oxide layer – H atoms are formed during the corrosion of $\text{Mg}_{17}\text{Al}_{12}$. Subsequently, H atoms formed during the corrosion of $\text{Mg}_{17}\text{Al}_{12}$ adsorb on the metal oxide surface and diffuse either on the oxide surface or on the metal surface. In fact, H diffusion is favorable on both the oxide and the intermetallic surface [16,20,21]. Since H atoms are formed in the corroded zone (MgO and Al_2O_3), the interaction of two H atoms on this surface is more probable than that on the non-corroded surface due to the smaller diffusion path. As a consequence, H_2 recombination and desorption is detected over the oxide surface. The variation of the other observed peaks is presented in Extended Data Fig. 6.

Huang *et al.* [37] stated that “Mg is first electrochemically oxidized to the intermediate active univalent Mg^+ ion on the Mg surface only in the film-free areas”. Nevertheless, Fig. 3e shows that the highest

intensity of H1 peak is in the film area (corroded surface) implying that Mg^+ and/or MgH^+ is formed in this zone. Moreover, it is supposed that the univalent Mg^+ reacts immediately with water converting into Mg^{2+} and producing hydrogen [37]. If this is true, H1 peak, attributed to the weakening of the H-H bond by Mg^+ [33,34] and/or MgH^+ [19], should not be detectable. In fact, this peak persists after the anodic polarization implying that Mg^+ and/or MgH^+ are chemically stable and does not immediately oxidize into Mg^{2+} .

4. Conclusion

In summary, our work clearly highlights the mechanism of H_2 production during the anodic polarization of $\text{Mg}_{17}\text{Al}_{12}$ in model sea-water solution (*i.e.* 3.5 wt.% NaCl).

- A mechanism of formation of H_2 during the corrosion of $\text{Mg}_{17}\text{Al}_{12}$ was proposed;
- H atoms formed on $\text{Mg}_{17}\text{Al}_{12}$ are adsorbed at the surface (Raman peak H2);
- H atoms then diffuse in the formed oxide layer and on the inter-metallic surface.
- A reaction intermediate (Mg^+ and/or MgH^+) is formed during the anodic polarization and weakens the standard H-H bond (Raman peak H1).
- The interaction of two H atoms on the oxide surface (more probable) or on the uncorroded surface (less probable) lead to the recombination and desorption of molecular H_2 .
- The mechanism of hydrogen production (*i.e.* H atoms generation, adsorption, diffusion, recombination and H_2 desorption) is experimentally proven by vibrational Raman spectroscopy.

Looking forward, we anticipate that our experimental results will also prove valuable when exploring the effect of monovalent Mg ion in the corrosion mechanism of metals and their alloys.

CRediT authorship contribution statement

S. Al Bacha: Methodology, Formal analysis, Investigation, Writing - original draft, Visualization. **A. Desmedt:** Validation, Investigation,

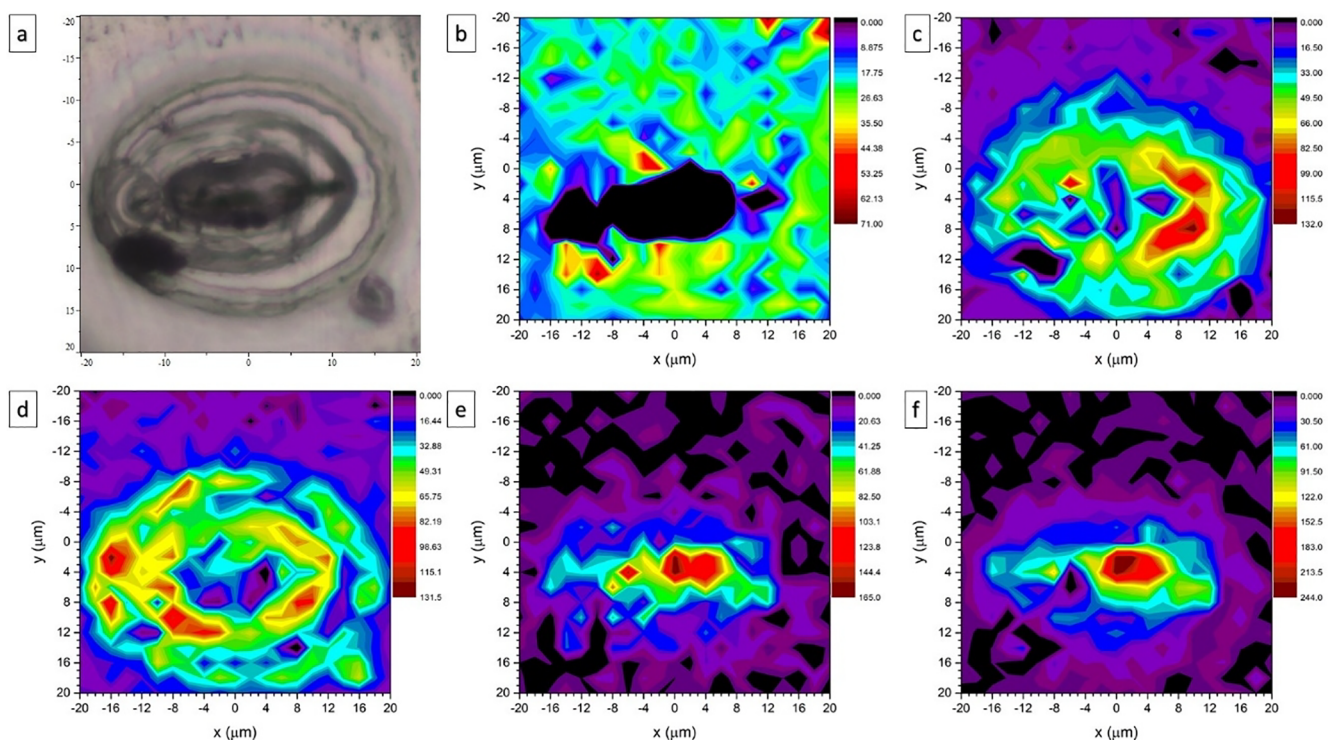


Fig. 3. a) Optical micrograph of the scanned area test and the variation of the intensity of the following peaks: b) $\text{Mg}_{17}\text{Al}_{12}$ ($700\text{--}900\text{ cm}^{-1}$), c) Mg ($960\text{--}1000\text{ cm}^{-1}$), d) MgO ($1030\text{--}1110\text{ cm}^{-1}$), e) H1 ($4015\text{--}4135\text{ cm}^{-1}$), and f) H2 ($4135\text{--}4255\text{ cm}^{-1}$).

Resources, Supervision. **M. Zakhour**: Validation, Project administration, Supervision. **M. Nakhli**: Validation, Project administration, Supervision, Funding acquisition. **J.-L. Bobet**: Conceptualization, Validation, Resources, Writing - review & editing, Project administration, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.elecom.2020.106813>.

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