

Research Article

Effect of Magnesium Hydride on the Corrosion Behavior of Pure Magnesium in 0.1 M NaCl Solution

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The effect of magnesium hydride on the corrosion behavior of pure magnesium in 0.1 M NaCl solution was investigated using the gas collection method, potentiostatic current decay test, and in situ Raman spectrum. The formation of magnesium hydride (MgH_2 , Mg_2H_4) was observed at the cathodic region. Applying anodic potential leads to decomposition of magnesium hydride. Magnesium hydride plays an important role on the negative difference effect (NDE) in both the cathodic and anodic regions.

1. Introduction

Magnesium is one of the lightest metals and its alloys have quite favorable properties which lead to specific applications. In particular, their high strength to weight ratio makes magnesium alloys extremely attractive for applications requiring light weight, such as transport and aerospace. However, magnesium alloys currently are still not as popular as aluminum alloys due to their poor corrosion resistant performance. Magnesium exhibits a very strange electrochemical phenomenon known as the negative difference effect (NDE) [1, 2]. Electrochemistry classifies corrosion reactions into anodic and cathodic processes. Normally, increasing the applied potential, the anodic reaction rate increases while the cathodic reaction rate decreases. Therefore for most metals like iron, steels, and zinc, and so forth, increasing the applied anodic potential will cause an increase of the anodic dissolution rate and simultaneously a decrease of the cathodic hydrogen evolution rate. However, the hydrogen evolution behavior on magnesium is quite different from that on iron and steels. Above the free corrosion potential, the hydrogen evolution rate increases with the increase of the applied nobler potential. Such behavior seems to be contradiction with the very basics of the electrochemical theory. NDE has been found on magnesium and aluminum, which are thermodynamically active [3]. The NDE is of critical importance for the corrosion of

magnesium [4, 5], including galvanic corrosion [6, 7] and stress corrosion cracking [8, 9]. Recently, the conception of NDE was extended to cathodic region by Song et al. [9]. Five typical models about NDE have been proposed: (a) partially protective surface film model; (b) monovalent magnesium ion model; (c) particle undermining model; (d) magnesium hydride model; (e) integration model which combines (a), (b), and (c). Thermodynamic data shows that the magnesium hydride could exist on an electrode surface [1]. The magnesium hydride could make a contribution to the NDE. Moreover, magnesium hydride could also reduce the mechanic strength of AZ91 due to the magnesium hydride cracking. According to the Pourbaix diagram of Mg- H_2O system calculated by Chen et al. [10], magnesium hydride could be formed by the following three electrochemical cathodic reactions:



In which the equilibrium potential for (1) is the lowest and that for (3) is the highest. This indicates that MgH_2 is easier to form through (2) and (3). In electrochemical

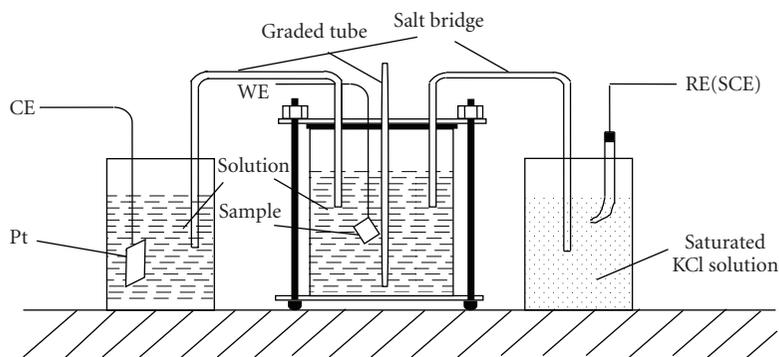
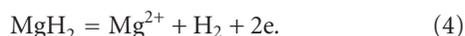


FIGURE 1: Sketch map of the apparatus for the hydrogen collection.

dynamics, it is well known that MgH_2 is not a stable compound, and it could decompose to Mg^{2+} and H_2 easily by the reverse reaction of (1):



Furthermore, the reverse reactions of (2) and (3) infrequently occur. Obviously, magnesium hydride would form by a cathodic reaction at a nobler potential and decompose by an anodic reaction at a lower potential. This will induce a new corrosion cell to be constructed in the $\text{Mg-H}_2\text{O}$ system. Since magnesium hydride is formed in a cathodic reaction, according to the electrochemical kinetic equation, the formation rate of MgH_2 should decrease as the applied potential approaches to the equilibrium potential of (3) or (2). However, the decomposition rate of MgH_2 should increase with the applied potential moving away from the equilibrium potential of (1). This brings confusion for understanding the effect of MgH_2 on NDE of Mg. And moreover, there are few in situ observations on testifying the existence of MgH_2 in $\text{Mg-H}_2\text{O}$ system.

The present work has focused on the effect of MgH_2 on the NDE of Mg corroded in 0.1 M NaCl solution. The existence of magnesium hydride was testified by the potentiostatic method combining the in situ observation by Laser Raman Spectrum. The advantages of using the Raman Spectrum in this study are the weak Raman scatter of water and no need for high vacuum; whereas other common surface analysis technology (e.g., XPS AES SIMS) had strict requirements on high vacuum. And hence, the Raman Spectrum could be monitored in real time while the magnesium sample is being corroded in the aqueous solution.

2. Experimental Procedures

2.1. Sample Preparation. The material studied in this experiment was pure magnesium (99.995 wt.%). The samples were embedded in epoxy resin, and the exposed surface area was 1 cm^2 . The sample surface was polished with 2000 grit SiC paper, cleaned with distilled water and acetone, and then dried in cold air.

2.2. Electrochemical Measurements. The corrosive medium was 0.1 M NaCl solution (pro analysis grade, $\text{pH} = 7.0$)

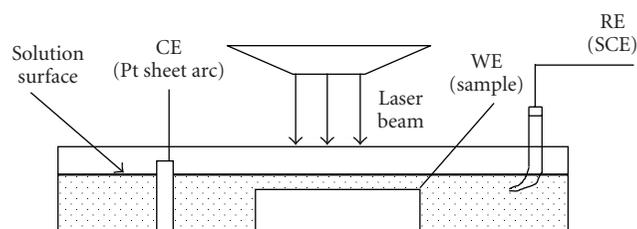


FIGURE 2: Sketch map of the apparatus for in-situ Laser Raman Spectrum detecting.

exposed in air at 25°C . A Potentiostat (Model 273A) was used to measure the current density decay through potentiostatic experiments. The working voltage ranged from -2.2 V/SCE to -0.8 V/SCE . For all the electrochemical tests a three-electrode system was employed, with pure magnesium as the working electrode, Pt plate as the auxiliary electrode, and the saturated calomel electrode (SCE) as the reference electrode. The amount of the evolved gas of hydrogen was measured simultaneously by a gas collection apparatus as illustrated in Figure 1. The greatest superiority of this apparatus is the capability to separate the outputting hydrogen from the corroding sample and those from the auxiliary electrode.

2.3. Laser Raman Spectrum Observation. A Jobin Yvon Horiba HR 800 LabRAM Raman microprobe was used for Raman spectra observation. The red light source with a wavelength of 632.8 nm was obtained from a He-Ne laser. The vibration spectra in the region between 50 and 2000 cm^{-1} were collected. The apparatus for Laser Raman Spectrum observation was illustrated in Figure 2. A three-electrode system was used in order to measure the spectra under different polarization potentials. The distance between the solution surface and the observed sample surface was 1 mm .

3. Results and Discussion

The results of the potentiostatic corrosion experiments for pure magnesium in 0.1 M NaCl solution are shown in Figure 3. The current density at all applied potential decays immediately to a constant value. The current density at

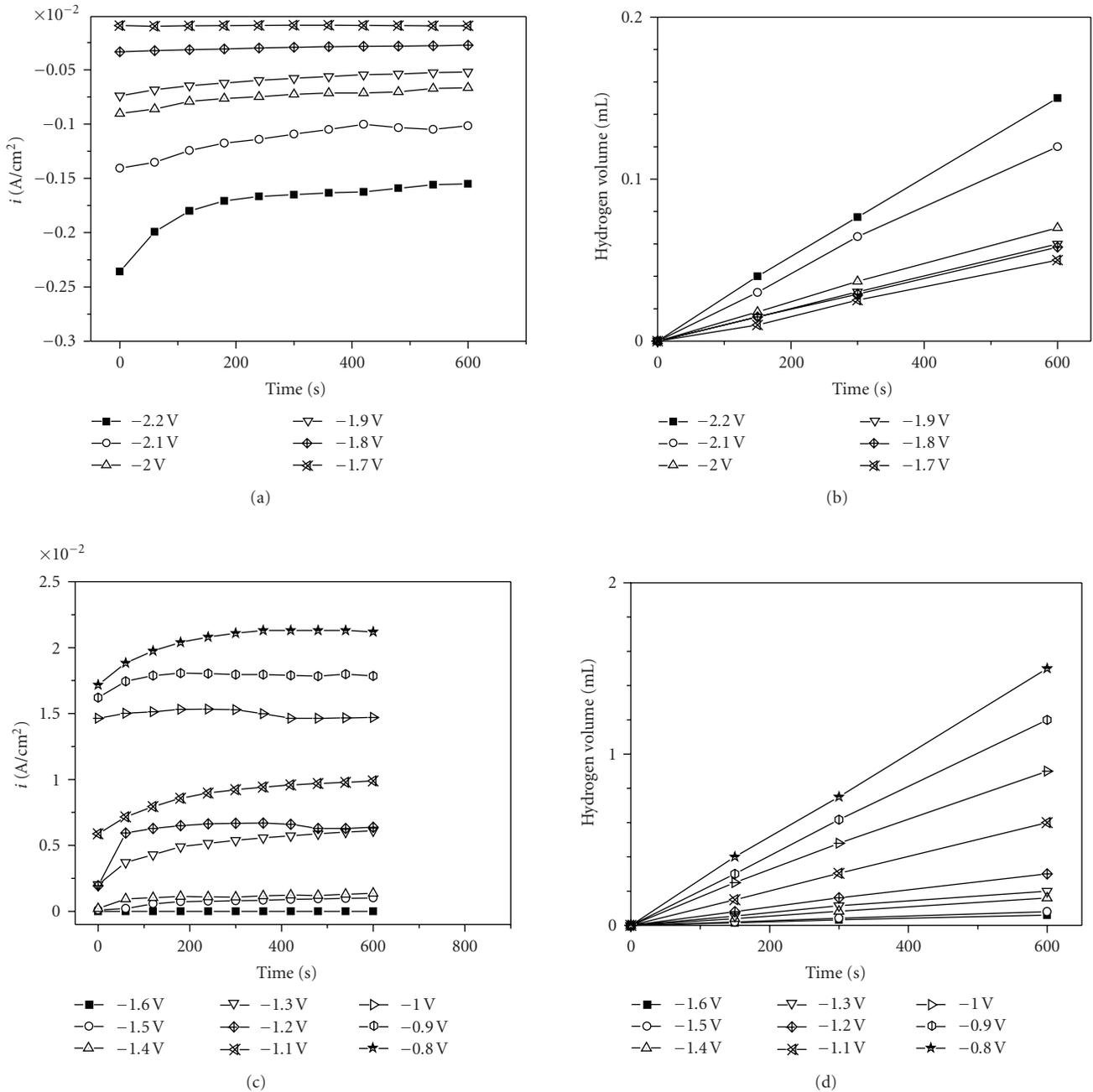


FIGURE 3: Current density and hydrogen generation of pure magnesium at different potentials in 0.1 M NaCl solution: (a) and (b) the cathodic process; (c) and (d) the anodic process.

any given time increases with the increase of the applied anodic potential, while decreases with the increase of the applied cathodic potential. The volume of the evolved gas increases linearly with time for both the anodic and cathodic processes. Furthermore, while increasing the anodic potential or decreasing the cathodic potential, the volume of H₂ also increases. Both the evolution rate of the volume of hydrogen gas and the current density stabilized after 300 second.

By assuming that the evolved gas obeys the model of ideal gas, the volume of gas evolution at each applied potential

within 300 s was converted to current density using the Faraday's law. Both the current densities calculated from the volume of the H₂ gas and those directly measured by potentiostatic experiments at each applied potential were plotted in Figure 4. The difference between the measured current densities and the calculated ones corresponding to each potential was also plotted in the same figure. There are three characteristic regions in the curves. The calculated current density is lower than the measured one in both the high anodic polarization region and the high cathodic polarization region. Nevertheless in the weak polarization

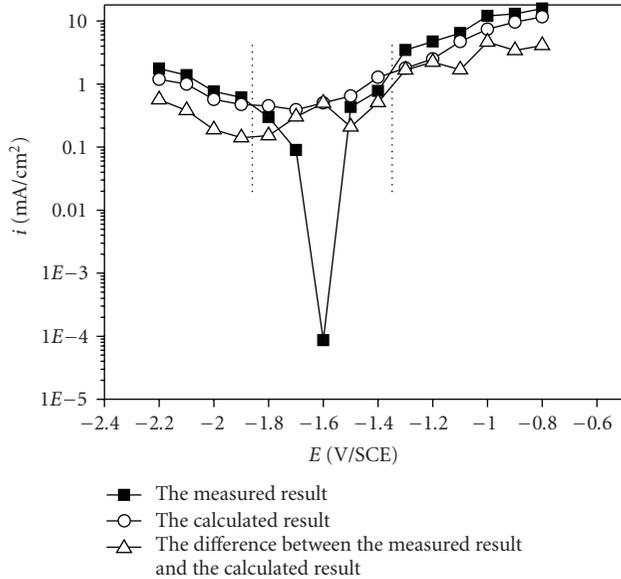


FIGURE 4: Polarized curve of pure magnesium in 0.1 M NaCl solution.

region, the calculated current density is slightly higher than the measured one.

In the cathodic region, if the reaction of H_2 evolution is the only cathodic process, the calculated polarization curve would be consistent with the measured polarization curve. The difference between the two curves implies that there was another cathodic reaction except H_2 evolution, that is, the formation of hydride besides hydrogen evolution. We assume that the anodic current density was so weak that it could be ignored in the high cathodic polarization region. Based on the possible corrosion reactions at the cathodic region and the Pourbaix diagram calculated by Chen et al. [10], I_c (the measured current density in the cathodic region) is composed of two parts: I_h which is caused by hydrogen evolution as expressed in reaction (5) and I_m that is caused by the formation of magnesium hydride as expressed from reactions (2) and (3). I_h could be calculated by the collected hydrogen gas volume using Faraday's law, and I_m could be expressed by the difference between I_c and I_h . The value of I_m represents the formation rate of the magnesium hydride. I_m increases with the decrease of the applied cathodic potential, which indicates that cathodic potential has important influence on the formation of magnesium hydride. Owing to the instability of magnesium hydride, it might decompose into magnesium hydroxide and hydrogen gas. But the formation rate of magnesium hydride is higher than the decomposition rate due to the large cathodic overpotential. It could be deduced that the formed magnesium hydride would affect the corrosion process of pure magnesium in the cathodic region.



In the anodic region, the effect of the cathodic current density on the external anodic current density is so weak that the cathodic current density could be ignored. The

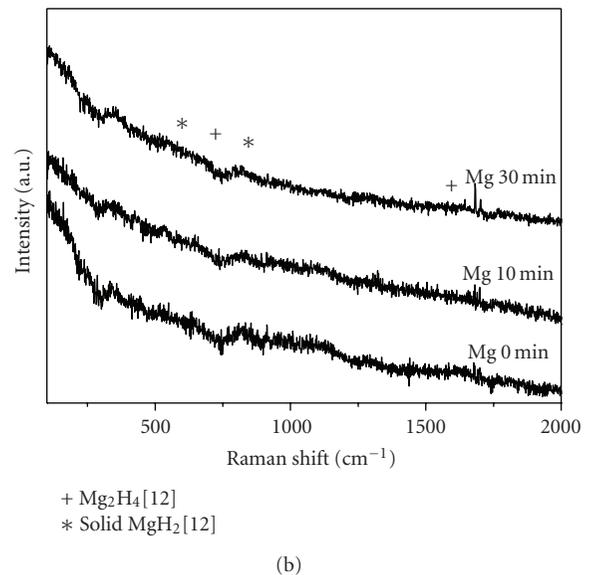
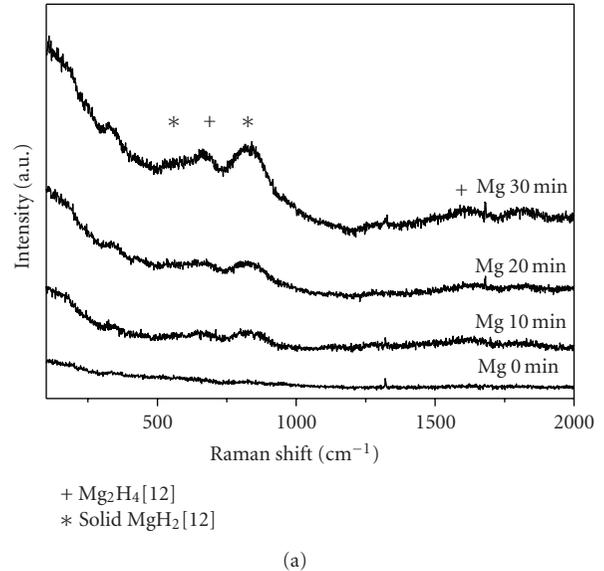
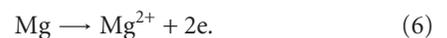


FIGURE 5: Comparison of Raman spectra for the pure magnesium polarized in 0.1 M NaCl solution for 30 minutes (a) -2.0 V/SCE (b) -0.8 V/SCE.

measured anodic current density I_a is consisted of two parts: I_m' which is caused by anodic hydrogen evolution, and I_n by anodic dissolution of Mg matrix. The calculated polarization curve of H_2 evolution reaction could be used for representing the negative difference effect of Mg; whereas the difference between the measured current density and the calculated current density could be used for representing the polarization curve of the anodic dissolution of Mg matrix as expressed in reaction



If the applied potential approaches the equilibrium potential of the formation of MgH_2 , the formation rate of the MgH_2 should get slower and slower until ceasing

at the equilibrium potential, and the NDE caused by the decomposition of MgH_2 should also stop at that time. However, it has been testified that the NDE continuously occur even if the applied potential exceeds the equilibrium potential of the formation of MgH_2 [10]. This indicates that the NDE of Mg is caused by not only the decomposition of MgH_2 (equation (4)) but also the reaction of the anodic evolution of H_2 . The monovalent magnesium ion model is used for explaining the extra contribution to NDE of Mg [11] as shown in

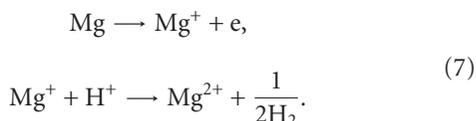


Figure 5 shows the Raman spectra of pure magnesium in 0.1M NaCl solution at a cathodic potential of -2.0 V/SCE and an anodic potential of -0.8 V/SCE, respectively. MgH_2 (830 and 560 cm^{-1}) and Mg_2H_4 (1587.6 and 667.2 cm^{-1}) were observed at cathodic polarization potential of -2.0 V/SCE. The spectra intensity of magnesium hydride increases with prolonging the cathodic polarizing time. The peaks at wavenumbers of 830 cm^{-1} and 560 cm^{-1} in the spectrum indicate the existence of the solid MgH_2 . The two wavenumbers are in good agreement with Infrared spectra of magnesium hydrides and density functional calculations [12]. For Mg_2H_4 , the wavenumber of 1587.6 cm^{-1} band is slightly higher than the Mg-H stretching mode of MgH_2 , which is appropriate for the terminal Mg-H stretching mode in Mg_2H_4 . The wavenumber of 667.2 cm^{-1} band arose from bending of bridge and terminal hydrogen atoms [12]. At high anodic polarization potential, no magnesium hydride band was observed in the Raman Spectrum. As mentioned above, the decomposition rate of MgH_2 increases with the increase of the applied potential, and simultaneously the formation rate of MgH_2 decreases with the increase of the applied potential. If the decomposition rate exceeds the formation rate of MgH_2 , there would be no extra MgH_2 on the surface of Mg matrix. Hence the characteristic Raman spectra of MgH_2 band will gradually weaken until disappearing. The detection of MgH_2 with in situ Raman spectra at the cathodic potential region is the evidence for the formation of Mg hydride which has been deduced by the results of Potentiostatic experiment previously. And the disappearance of the Raman spectra of MgH_2 at the anodic potential region testified the decomposition of MgH_2 .

In the weak-polarized region, the calculated current density is higher than the measured current density. Because the absolute value of the measured current is related to the difference between the current density of the anode and the cathode which could be written as $|I_a - I_c|$, while the calculated current density with the Faraday's law is derived with the sum of the evolved hydrogen volume from both the anodic and cathodic hydrogen evolutions. Hence, the calculated current density could be approximated as $|I_a| + |I_c|$. Therefore the calculated current density is higher than the measured current density in the weak-polarized region.

4. Conclusions

(1) It has been testified that the magnesium hydride (MgH_2 , Mg_2H_4) formed in the cathodic region and decomposed in the anodic region.

(2) Applying cathodic potential leads to the formation of magnesium hydride and applying anodic potential leads to the decomposition of magnesium hydride. The formation of magnesium hydride might contribute a part to the NDE of magnesium, and the reacting of the monovalent Mg^+ with H^+ might contribute another part to the NDE of magnesium.

Acknowledgments

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