Effects of Cadmium alloying on the Corrosion and Mechanical Properties of Magnesium

Shanna Xu¹, Magdalene Edet Ikpi^{1,2}, Junhua Dong^{1,*}, Jie Wei¹, Wei Ke¹, Nan Chen¹

¹ State Key Laboratory for Corrosion and Protection, Institute of Metal Research, Chinese Academy of Sciences, China.

² Department of Pure and Applied Chemistry, University of Calabar, Nigeria.

^{*}E-mail: <u>jhdong@imr.ac.cn</u>

Received: 2 April 2012 / Accepted: 21 April 2012 / Published: 1 May 2012

The effect of Cd on the corrosion-resistant behavior and mechanical performance of Mg using gas collection, electrochemical measurements and tensile stress tests has been investigated. The experimental results showed that in the cathodic polarized region, hydrogen evolution and magnesium hydride formation were significantly reduced, whereas in the anodic polarized region, the negative difference effect was restrained and the anodic dissolution slightly enhanced when Cd (2.04 wt.%) is alloyed to Mg. The sum effect of the cathodic and anodic reactions results in an improvement of the corrosion resistant behavior in Mg-Cd alloy. Furthermore, the addition of Cd has been found to reduce the susceptibility to stress corrosion cracking. The mechanisms of these improved properties has been clarified by considering the formation of a stable Mg^{v+} - Cd^{δ -} galvanic couple in the Mg-Cd alloy that can be applied in the interpretation of the corrosion behavior of other Mg alloys.

Keywords: Magnesium-cadmium alloy; Corrosion resistance; Negative difference effect; Magnesium hydride; Mechanical properties

1. INTRODUCTION

Magnesium and its alloys are an excellent choice for lightweight structural applications in the automotive and aerospace industry. These materials exhibit desirable characteristics of high specific strength, low density, excellent castability, damping ability, and ease in machining [1-3]. Yet one major problem with the application of Mg and its alloys as structural materials is its poor corrosion resistance in moderately aggressive environments [4-8]. In addition, the increasing use of Mg alloys in structural load-bearing applications where the effects of stress corrosion cracking are obvious [9], makes it imperative to design Mg alloys that possess excellent mechanical properties.

The corrosion of Mg and its alloys display an unusual phenomenon of increasing hydrogen evolution with increasing potential known as Negative difference effect (NDE). It is of crucial significance in the study of the corrosion behavior of Mg and its alloys [10,11] as it causes severe damage and defects by shortening the lifetime of materials under corrosive environments due to the formation of galvanic corrosion [12,13] and stress corrosion cracking [14]. It is therefore essential in the study of the corrosion behaviour of Mg and Mg alloys to understand the mechanism of the corrosion processes with a view to reducing the NDE behaviour. Although the interpretation of NDE induced by monovalent magnesium ion (Mg⁺) [15-21] is increasingly acknowledged, the mechanism through which NDE is induced by the decomposition of magnesium hydride still remains unclear and debated [22-24]. Interestingly, as evidenced via various experimental measurements, MgH₂ has been found to exist in the film of magnesium corrosion products [25-27], and its formation is supported by thermodynamic theoretical analysis [28]. In addition, the formation of MgH₂ in the cathodic region is known to degrade the mechanical properties of Mg alloys [29], while NDE in the anodic region is associated with cracking and subsequent disintegration of magnesium [30]. Generally, the presence of hydrogen in the corrosion system of Mg and its alloys has been linked with stress corrosion cracking caused by hydrogen embrittlement in the alloy [29,31,32]. However, in recent years, the perception of the NDE phenomenon has continued to evolve with new ideas. The uncertainty concerning the existence of the uni-positive Mg^+ ion [33], the observation of a magnesium dissolution stoichiometry of approximately of n = 2 [34], the understanding of NDE as a consequence of a localized corrosion mechanism involving hydrogen evolution due to cathodic activation [35] and the explanation of NDE as showing that the corrosion of Mg and its alloys are dependent on two electron consuming processes resulting from external polarization measured as current flow on the ammeter and from hydrogen gas formation [36]; are all a testament to the continued interest in the understanding of NDE.

An attempt at identifying an effective way to reducing significantly the formation of both magnesium hydride and the monovalent magnesium ion in Mg and its alloys will present solutions to greatly improving the corrosion resistance and mechanical performance of these materials. Mercury has been reported to reduce the hydrogen evolution reaction (HER) rate [37]. This is attributed to the nature of its droplet having a very high over potential and a low exchange current density during the reduction of H⁺ [38]. Nonetheless, mercury addition degrades the mechanical performance [39]. Interestingly, Zn, Cd and In possess properties similar to those of Hg for H⁺ reduction [38]. Of all the mercury-like metals, Cd readily dissolves into Mg phase forming a mutual solid solution above 253 °C. Even at a lower temperature, the phase diagram of Mg-Cd alloy exhibits a region in which a complete solid solution was observed with the maximum of 20 atomic percent Cd [40-42]. In comparison with other elements, the solubility of Cd in Mg is the largest [43] and this helps in reducing the formation of intermetallic phases. The addition of Cd has been found to increase significantly the tensile strength of Mg [44]. Also, its effect in reducing the HER of Mg alloy has been partly proven [45]. The foregoing implies that the addition of Cd to Mg would have both the desirable effects of improving the corrosion resistance and enhancing the mechanical strength of Mg.

In furtherance to our research on the corrosion behavior of Mg alloys, we present herein a systematic investigation of the effect of alloyed Cd to Mg using gas collection and electrochemical techniques. Our interest is focused on the role of Cd in the reduction of NDE and in the understanding

of the formation of magnesium hydride for improved corrosion resistance and mechanical strength in Mg alloys. We report a remarkable improvement in the corrosion resistance and mechanical properties of Mg alloyed with Cd. Furthermore, we have explained the anodic and cathodic reactions taking place on the metal surface from an atomic perspective using a micro-galvanic couple model that is for the first time reported in literature. The results demonstrate the benefit of Cd incorporation in the design of new corrosion resistant Mg alloys for enhanced engineering use.

2. EXPERIMENTAL

2.1. Sample preparation

The materials used for the experiments were Magnesium (Mg) and as-cast Magnesium-Cadmium (Mg-Cd) alloy. The Mg alloy was prepared from pure Mg (99.995 wt.%) with impurities, Fe ≤ 100 ppm and Ni ≤ 50 ppm. The chemical composition of the as-cast Mg-Cd alloy was 2.04 wt.% Cd and the balance Mg with impurity levels of Fe ≤ 100 ppm and Ni ≤ 50 ppm. The chemical compositions of the materials were measured by inductively coupled plasma atomic emission spectroscopy. The alloy was first smelted by adding cadmium (99.99 wt.%) to magnesium (99.995 wt.%) in a shaft crucible furnace in the presence of CO₂ and SF₆ gases at a temperature of 750 °C , followed by casting in a water-cooled graphite mould.

The samples were cut into dimensions of $(10 \times 15 \times 2)$ mm³ for the immersion test, whereas those for the electrochemical tests were mounted using epoxy resin with 1 cm² surface exposed. The samples were ground with 2000 grit SiC paper, cleaned with distilled water and acetone and dried in cold air.

2.2. Structure and surface identification

The structural identification of the materials were characterized by means of X-ray diffraction (XRD) by employing a D/Max-2500PC detecting machine ($\lambda_{Cu \ Ka} = 1.54$ Å). The corrosion morphologies were observed using a Phillips XL30 scanning electron microscope (SEM) equipped with energy dispersive X-ray analysis (EDS). All samples were sprayed with thin gold films to create a conducting surface. In order to observe the corrosion features clearly, the corrosion products that formed after the immersion test on pure Mg and Mg-Cd alloy were removed in a hot chromic acid bath consisting of 180 g/L CrO₃. A conventional optical microscope was used to obtain metallographic images of the alloy.

2.3. Immersion test and electrochemical measurements

The samples for the immersion test having a dimension of $(10 \times 15 \times 2)$ mm³ were completely immersed in 400 mL 0.1 mol L⁻¹ NaCl solution at pH = 7 for 24 hours at open circuit potential (OCP) under a room temperature of 25 °C. An experimental arrangement as described by Song et al [46]. was used to collect and measure the hydrogen gas that evolved during the immersion test. The hydrogen evolution rate H_R (ml/cm²/d), was determined and related to the corrosion rate CR_H , in (mm/y) using the expression below.

$$CR_{\rm H} = 2.279 \ \rm H_R \tag{1}$$

Electrochemical Impedance Spectroscopy (EIS) measurements were carried out at open circuit potential on epoxy-mounted samples having 1 cm² surface exposed at various times up to 24 hours. The samples were ground using 2000 grit SiC paper, cleaned with distilled water and acetone and dried in cold air prior to EIS measurements in 0.1 mol L⁻¹ NaCl solution using a M273A/5210E Potentiostat/Phase-lock amplifier over the frequency range of 100 KHz to 10 mHz with an AC amplitude perturbation of 5 mV. A three-electrode electrolytic cell set-up having Mg and Mg-Cd alloy as the working electrode, Pt plate as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode was used. The potentiodynamic polarization curves were measured at a constant sweeping rate of 0.2 mV/s. For the potentiostatic polarization test, the working electrode potential ranged from -2.200 V/SCE to -0.800 V/SCE. The current density and the volume of the hydrogen gas evolved at each applied potential were simultaneously measured for 600 s using the potentiostat and a gas collection apparatus [20] respectively. The polarization resistance R_p , was evaluated from the EIS results as the value of the impedance at 1 Hz at final immersion (24 hrs) and was used to derive an estimate of the corrosion current density i_{corr} (mA/cm²) [47]; calculated using values of the cathodic Tafel slope β_c , and anodic Tafel slope β_a , from polarization curves. The corresponding corrosion rate P_i (mm/y) was evaluated using [48].

$$i_{corr} = \frac{B}{R_p} \tag{2}$$

where,

$$B = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \tag{3}$$

$$P_i = 22.85 i_{corr} \tag{4}$$

2.4. Differential Scanning Calorimetry (DSC) measurements

Mg and Mg-Cd alloy specimens having a dimension of $(10\times10\times0.1)$ mm³ were potentiostatically polarized at a potential of -2.000 V/SCE for 24 hours in 0.1 mol L⁻¹ NaCl solution for cathodic hydrogenation to occur. The magnesium hydroxide film [49] (produced by the dissolution of both Mg matrix and magnesium hydride) on the charged specimen was removed in 180 g/L CrO₃ solution, the specimen was cleaned with distilled water and acetone and finally dried in cold air. A DSC (Pyris DSC404) testing machine operating at a heating rate of 20 °C/min was employed to detect the thermal desorption behavior of magnesium hydride formed during the cathodic polarizing processes of the specimens. All measurements were performed in standard alumina cups and under a constant flow rate of 200 mL min⁻¹ of pure argon (purity > 99.999 %) to prevent oxidation. The proportion of magnesium hydride desorbed was calculated by integrating the peak area under the DSC curves.

2.5. Stress Corrosion Cracking (SCC) susceptibility evaluations

A Shimadzu AGX-20kN universal tensile machine was employed in order to detect the SCC susceptibility of Mg and Mg-Cd alloy using the slow strain rate test (SSRT) method. The sheet tensile specimen had a gauge dimension of 15 mm (length) \times 5 mm (width) \times 2.5 mm (thickness). Before the SSRT test, the tensile samples were polished using SiC paper with grit size up to 5000 (produced by RIKEN Corp.), rinsed in distilled water and cleaned with ethanol.

The tests were performed under conditions of laboratory atmosphere (air) and in 0.1 mol L⁻¹ NaCl solutions at a strain rate of 10^{-6} s⁻¹. The immersion length of each specimen in the test solution was 15 mm. For the tests conducted in solution, three different potential settings of -2.000 V/SCE (cathodic), open circuit potential (OCP) and +50 mV/OCP (anodic) were used. The SCC susceptibility was evaluated by the parameters of ultimate tensile strength (UTS), elongation to failure (ε_f), and the reduction of area (RA). The SCC susceptibility was further characterized by a parameter A, which is the percentage ratio of the tensile stress of the specimen measured in the test solution at a particular polarized condition to its corresponding measurement in air. Thus, A_{UTS} (%) is the percentage ratio of the specimen in the test solution measured in MPa to its corresponding tensile stress measurement in air. The same applies to A_{ef} (%) and A_{RA} (%).

3. RESULTS

3.1. Microstructure

Fig. 1 shows the XRD patterns of Mg and Mg-Cd alloy. It indicates that Mg-Cd alloy is isostructural to α-Mg matrix [50]. The results confirm a solid solution in Mg-Cd alloy in accord with the binary phase diagram of Mg-Cd [40-42]. The metallography of Mg-Cd alloy (Fig. 2a) shows no evidence of intermetallic particles and the grain sizes of the alloy are large with dimensions of about 1-2 mm. Thus, the grain size effect on the corrosion process could be neglected safely in the present study. Furthermore, Fig. 2b presents the SEM image of Mg-Cd alloy with its corresponding EDS maps for Mg (Fig. 2c) and Cd (Fig. 2d). The microstructure of Mg-Cd alloy reveals an even distribution of Cd in the Mg matrix and no intermetallic particles were observed.



Figure 1. X-ray diffraction patterns of pure Mg and Mg-Cd alloys.



Figure 2. (a) A metallographic image of Mg-Cd alloy, (b) SEM image, (c) & (d) the corresponding EDS maps for Mg and Cd respectively for the alloy.

3.2. Hydrogen gas collection and polarization curves

The corrosion rates CR_H , calculated from the volume of hydrogen evolved during the immersion test was 1.06 mm/y for Mg-Cd alloy and 3.44 mm/y for pure Mg. The corrosion rate of Mg-Cd alloy was found to be less than a third the corrosion rate of pure Mg. Fig.3 shows the

polarization curves of pure Mg and Mg-Cd alloy measured in 0.1 mol L⁻¹ NaCl solution. The plot reveals an increase in the apparent anodic Tafel slope β_a in the Cd containing sample, whereas the apparent cathodic Tafel slope β_c of both pure Mg and Mg-Cd are similar. Moreover, the plot presents a decrease in both the anodic and the cathodic current densities of Mg-Cd alloy. The increase in the gradient of the Tafel slope and the decrease in the current densities mean the reactions in both anodic and cathodic regions are restrained by Cd addition. The OCP values for Mg and Mg-Cd alloy were -1.584 V/SCE and -1.606 V/SCE respectively. The OCP shifted in the negative direction with Cd addition. For magnesium alloys, there is no quantitative relation between the corrosion potential E_{corr} to the corrosion rate [18].



Figure 3. Potentiodynamic polarization curves of Mg and Mg-Cd alloy in 0.1 mol L⁻¹ NaCl solutions at pH 7 and 25 °C.

3.3. EIS spectra

The Nyquist plots of Mg and Mg-Cd alloy in Fig. 4a and 4b respectively, show the impedance at initial immersion as composed of two capacitive loops; a high frequency (HF) loop, caused by the charge and discharge of the electric double layer and a low frequency (LF) loop caused by the film capacitance.

The Bode-|Z| plots of Mg and Mg-Cd alloy in Fig. 4a' and 4b' clearly show the existence of these two capacitive loops at initial immersion. Likewise, the Bode-phase plots (Fig. 4a'' and 4b'') expresses these loops with both having positive phase angles. After 2 hrs immersion, the HF capacitive loop shrinks and one inductive loop starts to appear in the LF range, and is equally seen in Fig. 4a'' and 4b'' having a positive phase angle and a negative phase angle respectively. This change can be attributed to the dissolution of films and the occurrence of localized corrosion [51,52].



Figure 4. EIS plots of pure Mg (a, a', a'') and Mg-Cd alloy (b, b', b'') after varied times of immersion in 0.1 mol L⁻¹ NaCl solutions at pH 7 and 25 °C.

Mg-Cd alloy is found to exhibit a lower resistance to corrosion than pure Mg at initial immersion, but higher at final immersion (24 hrs) at low frequencies (f = 0.01 Hz) as seen in Fig. 4a' and 4b'. For Mg, the impedance significantly decreased to about 200 ohm cm² at 4 hr, and then continuously dropped down to about 50 ohm cm² at the final immersion time. The impedance for Mg-Cd alloy also decreased with increasing immersion time, but not as severe as Mg, reaching a minimum of about 200 ohm cm² after 16 hrs immersion. A lower corrosion resistance for Mg is mainly related to severe localized corrosion and higher corrosion rate. The values of *B* calculated from Eq. (3) using values of β_c and β_a obtained from the polarization curves are 19.3 mV and 13.3 mV for Mg-Cd alloy and pure Mg respectively. The impedance value at 1 Hz was stochastically chosen as the polarization resistance R_p since about this frequency the impedance values appear relatively stable. Thus, R_p

measured 560 ohm cm² for Mg-Cd and 120 ohm cm² for Mg at final immersion (24 hrs). The estimated current densities are 0.034 mA/cm² and 0.110 mA/cm² for Mg-Cd alloy and Mg respectively. The converted corrosion rate for Mg-Cd alloy is 0.78 mm/y and 2.53 mm/y for Mg. It is evident that the corrosion rate of Mg-Cd alloy is significantly lower than that of pure Mg. The results from the EIS and polarization curves are consistent with the corrosion rates obtained from hydrogen gas collection. In addition, the corrosion rate of Mg determined via hydrogen evolution was observed to be higher than that of Mg-Cd alloy by a factor of about 3.2, while the corrosion rate for Mg from both polarization and EIS measurements differed by a factor of 3.1 times that for Mg-Cd alloy. The improvement in the corrosion resistance of Mg-Cd alloy as shown by the lower corrosion rates in the experimental data demonstrates the potential of Cd in improving the corrosion performance of Mg.

3.4. Corrosion morphologies

Fig. 5a and 5b show the SEM images of the corroded surfaces and Fig. 5c and 5d the crosssectional views of pure Mg and Mg-Cd alloy respectively after 24 hrs immersion in the test solution. Localized form of corrosion was observed on Mg surface and the extent of damage was widespread, while uniform corrosion was expressed on Mg-Cd alloy with relatively lesser area of damage to its surface.



Figure 5. Scanning electron micrographs of (a) & (b) the surface, and (c) & (d) the cross-sections of pure Mg and Mg-Cd alloy respectively after immersion for 24 hrs in 0.1 mol L⁻¹ NaCl solution at 25 °C and pH 7.

Int. J. Electrochem. Sci., Vol. 7, 2012

The surface of Mg-Cd alloy shows uniformly shallow scars, whereas the surface of pure Mg exhibits deep scars, evidenced by the penetration depth of about 400 μ m of the corrosion product on Mg (Fig. 5c), and about 20 μ m on Mg-Cd alloy (Fig. 5d) as seen on the cross-sectional images of these samples. The extent of pitting on the surface of both Mg and Mg-Cd alloy after subjecting the samples to strain test under anodic polarization is shown in Fig. 6. The degree of pitting is greater in the Mg sample with the pits merging together to form deep cracks on the surface indicative of localized corrosion, whereas fewer pits typical of pitting corrosion are observed on the surface of Mg-Cd alloy.



Figure 6. Stereomicroscope photos of (a) pure Mg, and (b) Mg-Cd alloy showing the extent of pitting on the surface.

3.5. Potentiostatic current decay results

Fig. 7 and Fig. 8 show the potentiostatic polarization results measured for pure Mg and Mg-Cd alloy respectively in 0.1 mol L^{-1} NaCl solutions. It can be seen from the results of both Mg (Fig. 7a and 7c) and Mg-Cd alloy (Fig. 8a and 8c) that the time-dependent current density is immediately decayed to a constant value at various potentials [53,54]. The results show that the current density reaches a stable state just after 300 s polarization. The cathodic current density decreases with enhancing cathodic potential, whereas the anodic current density increases with increasing anodic polarized potential. The evolved gas volume linearly increases with time, and increases with decreasing cathodic potential and with increasing anodic potential.

The evolved gas volume, if obeying the ideal gas law, can be converted to a current density value using Faraday's law. A comparison of the current densities measured from the potentiostatic experiment (i_c and i_a), converted from the evolved gas volumes (i_H and $i_{H'}$) and their differences (i_m and $i_{m'}$), with potential for the cathodic and anodic processes respectively is presented in Fig. 9. In high anodic or in the high cathodic polarized regions, a pure anodic or cathodic current density respectively can be reasonably assumed to be the external current density.



Figure 7. (a) & (c) - the variation of current density with time and (b) & (d)- the variation of volume of hydrogen evolved with time for pure Mg at different potentials in 0.1 mol L^{-1} NaCl solution at 25 °C and pH 7. (a) and (b) represent the cathodic process while (c) and (d) represent the anodic process. All potentials are with respect to the Saturated Calomel Electrode (SCE).



Figure 8. (a) & (c) - the variation of current density with time and (b) & (d)- the variation of volume of hydrogen evolved with time for Mg-Cd alloy at different potentials in 0.1 mol L⁻¹ NaCl solution at 25 °C and pH 7. (a) and (b) represent the cathodic process while (c) and (d) represent the anodic process. All potentials are with respect to the Saturated Calomel Electrode (SCE).

However, the converted current density is obviously less than the measured current density for both the high anodic and the high cathodic polarization regions for all of the specimens. Furthermore, the hydrogen evolution on Mg-Cd is much lower than that on Mg, indicating that Cd alloying can control the hydrogen evolution process in the cathodic region and the negative difference effect (NDE) in the anodic region. Additionally, in the cathodic region the difference between the measured and converted current densities in pure Mg is larger than in Mg-Cd alloy, while in the anodic region the difference is smaller in Mg than in Mg-Cd alloy.



Figure 9. The polarization curves of pure Mg and Mg-Cd alloy in 0.1 mol L⁻¹ NaCl solutions at 25 °C and pH 7 showing the measured current densities (i_c and i_a), the converted current densities (i_H and $i_{H'}$), and their difference (i_m and $i_{m'}$) for (a) the cathodic process, and (b) the anodic process (standard error within 5%).

3.6. Magnesium hydride detection

The use of DSC in detecting magnesium hydride has been largely employed in the area of magnesium-based hydrogen storage research [55,56]. We believe that it is appropriate in this research to verify the formation of magnesium hydride under cathodically polarized conditions. Fig. 10 shows the DSC curves of Mg and Mg-Cd alloy after potentiostatic polarization at -2.000 V/SCE for 24 hrs in 0.1 mol L⁻¹ NaCl solution. The decomposition peaks for magnesium hydride in pure Mg and Mg-Cd alloy were detected in a temperature range of 350-400 °C, and is consistent with the results reported by Gerasimov [55] and Fátay [56]. The dehydrogenation reaction of Mg-Cd alloy starts at 350 °C, which is higher than that of pure Mg by about 40 °C. This difference can be ascribed to the fact that the concentration of magnesium hydride distributing in Mg-Cd alloy is indeed lower than that in pure Mg.



Figure 10. DSC curves of Mg and Mg-Cd alloy after charging at -2.000 V/SCE for 24 hrs in 0.1 mol L⁻¹ NaCl solution.

The decomposition energy of magnesium hydride formed in the cathodically charged Mg or Mg-Cd alloy can be calculated from the integration area of the endothermal peaks. Following this rule, the endothermal heat of the cathodically charged specimen of Mg-Cd alloy is 12.78 J/g, which is much lower than that of the pure Mg specimen of 58.63 J/g. The decomposition enthalpy (Δ H) of MgH₂ is - 74 kJ/mol [56], thus the content of magnesium hydride cathodically formed in the specimens of Mg-Cd alloy and in pure Mg can be deduced by the ratio of its decomposition energy to the decomposition enthalpy of MgH₂. The calculated values are 4488 ppm for Mg-Cd alloy and 20592 ppm for pure Mg. These values clearly prove that alloying Cd to Mg matrix significantly restrains the formation of magnesium hydride. These results are consistent with *In-situ* Raman spectrum results of another Mg-Cd alloy of different Cd composition [54] where a higher concentration of magnesium hydride was detected on Mg than on the Mg-Cd alloy.

3.7. Effect of Cd on SCC behavior

The stress-strain curves for pure Mg and Mg-Cd alloy in air and in 0.1 mol L⁻¹ NaCl solution at anodic, cathodic and open circuit potentials, measured at a strain rate of 10^{-6} s⁻¹ are shown in Fig. 11. The tensile stress parameters are listed in Table 1 with values given in terms of the ultimate tensile strength (UTS), elongation to failure (ε_{f}), reduction of area (RA) and the parameter A. The values of the tensile stress measured in terms of UTS, ε_{f} and RA show agreement in all test environments for both samples. The parameter A generally shows higher values for Mg-Cd alloy than for pure Mg. A higher value of the parameter A indicates lower SCC susceptibility. A higher SCC susceptibility in air and in 0.1 mol L⁻¹ NaCl solution at all potentials studied is observed in pure Mg than in Mg-Cd alloy as shown in Fig. 11 and in Table 1. Both samples present the highest tendency to undergo SCC under anodic polarized conditions compared to other test environments.



Figure 11. Stress versus apparent strain curves for Mg and Mg-Cd alloy measured in air, and in 0.1 mol L^{-1} NaCl solutions under open circuit potential, cathodic polarization and anodic polarization. (See Table 1 for values of the electrode potentials of the specimens at OCP, cathodic polarization and anodic polarization).

Within the cathodically charged samples, hydrogen diffuses into the sample, reacts with Mg forming magnesium hydride as the corrosion product. It is accepted that magnesium hydride plays an important role in the SCC of Mg and this is evidenced in a number of research reports [26,57-59]. Due to the synergistic effect of high-local pressure and expansion stress caused by the formation of brittle magnesium hydride, the material would easily crack [29,30].

Sample in	Polarization	Tensile test parameters				*A (%)	
environment	potential	UTS	\mathcal{E}_{f}	RA	A_{UTS}	$A \mathcal{E}_{f}$	A _{RA}
	(V/SCE)	(MPa)	(%)	(%)	(%)	(%)	(%)
Mg in air		75	9.2	7.8			
Mg in test	-2.000 (Cathodic)	63	6.3	5.4	84.0	68.5	69.2
solution	-1.584 (OCP)	66	6.5	5.6	88.0	70.7	71.8
	-1.534 (Anodic)	33	4.0	3.1	44.0	43.5	39.7
Mg-Cd in air		116	11.2	9.4			
Mg-Cd in test	-2.000 (Cathodic)	103	7.7	6.9	88.8	68.8	73.4
solution	-1.606 (OCP)	110	7.8	7.1	94.8	69.6	75.5
	-1.556 (Anodic)	74	5.4	5.0	63.8	48.2	53.2

Table 1. Tensile test parameters of pure Mg and Mg-Cd alloy tested in air and in 0.1 mol L⁻¹ NaCl solutions under cathodic polarization, open circuit potential (OCP) and anodic polarization.

A (%) is the percentage ratio of the tensile stress of the specimen measured in the test solution at a particular polarized condition to its corresponding measurement in air.

After a cathodic charging, many micro-cracks are initialized when the hydride size or hydrogen concentration reaches some certain critical values. The lower SCC susceptibility in Mg-Cd alloy than in pure Mg is attributed to the lower hydrogen evolution and a lesser magnesium hydride formation in

Mg-Cd alloy under cathodic polarization. The occurrence of a lower susceptibility to SCC in Mg-Cd implies that there is significant improvement in its mechanical performance over that of pure Mg.

Under anodically charged conditions, the SCC behavior is controlled by a number of processes namely anodic dissolution, pitting and hydrogen embrittlement. In Mg-Cd alloy, the material experiences a lower pitting tendency as seen in Fig. 6 and a lower NDE, although it shows a higher anodic dissolution rate. We believe that the lower SCC susceptibility occurrence in Mg-Cd alloy may be ascribed to a lower pitting tendency and a lower NDE of which the combined effect outweighs the consequence of the increased anodic dissolution rate observed in the alloy.

4. DISCUSSION

4.1. Effects of Cd addition

On the cathodic reactions:

In the cathodic region, the difference between the measured and converted current densities for Mg and Mg-Cd alloy can be ascribed to the fact that the cathodic process consists of two reactions, a hydrogen evolution reaction and a magnesium hydride formation [10,21]. Based on thermodynamic considerations, the monovalent magnesium ion model may also play a role in releasing hydrogen in the cathodic region due to its low equilibrium potential (-2.659 V/NHE) [28] and strong reducibility. Since the formation of the monovalent magnesium ion is an anodic reaction and that the anodic current is so weak in the region of high cathodic polarization, it could be disregarded. Thus, in order to simplify the discussion, the effect of monovalent magnesium ion is ignored in the cathodic region.

The measured cathodic current density i_c , is assumed to comprise two parts; i_H , induced by hydrogen evolution (Eq. 5) and i_m , caused by the formation of magnesium hydride (Eq. 6). i_m can thus be expressed as the difference between i_c and i_H .

$$\mathrm{H}^{+} + \mathrm{e}^{-} \to \frac{1}{2} \mathrm{H}_{2} \tag{5}$$

$$Mg + 2H^{+} + 2e^{-} \rightarrow MgH_{2}$$
(6)

Following electrochemical kinetics, i_c reads;

$$|i_{c}| = i_{H} + i_{m} = i_{0,c1} \exp\left[-\frac{E - E_{e,c1}}{\beta_{c1}}\right] + i_{0,c2} \exp\left[-\frac{E - E_{e,c2}}{\beta_{c2}}\right]$$
(7)

where $i_{0,c1}$ is the cathodic exchange current density of hydrogen evolution, $i_{0,c2}$ the cathodic exchange current density of magnesium hydride formation, β_{c1} and β_{c2} , both components of β_c the cathodic Tafel slope while $E - E_{e,c1}$ and $E - E_{e,c2}$, are both components of $E - E_{e,c}$ the over potential. Evidently, i_c depends on the parameters $i_{0,c1}$, $i_{0,c2}$, β_c and $E - E_{e,c}$. Indeed, i_m increases with decreasing the applied potential (Fig. 9). This demonstrates that the occurrence of magnesium hydride is a result of a cathodic electron transfer reaction. Both i_H and i_m of Mg-Cd alloy are thus much less than those of pure magnesium since the addition of Cd limits the formation of both hydrogen and magnesium hydride. A similar fact has been reported in the decrease of the hydrogen storage capacity of Mg-Cd alloys with increasing Cd content due to the restrained magnesium hydride formation [60].

On the anodic reactions:

In the high anodic region, the cathodic current density is so weak and it can be ignored. The measured anodic current density i_a , consists of two parts; $i_{H'}$, caused by hydrogen evolution a consequence of NDE and $i_{m'}$, caused by the anodic dissolution of the matrix. As before, $i_{m'}$ is the difference between the measured and converted current densities. The difference between the measured and converted current densities implies that the anodic process simultaneously involves an anodic dissolution of the metal and a hydrogen evolution reaction [11]. According to electrochemical kinetics, i_a can be expressed as:

$$\left|i_{a}\right| = i_{H'} + i_{m'} = i_{0,a1} \exp\left[\frac{E - E_{e,a1}}{\beta_{a1}}\right] + i_{0,a2} \exp\left[\frac{E - E_{e,a2}}{\beta_{a2}}\right]$$
(8)

The terms $i_{0,a1}$ and $i_{0,a2}$ are the anodic exchange current density of hydrogen evolution and the anodic exchange current density of the dissolution of Mg respectively, β_{a1} and β_{a2} , both components of β_a the anodic Tafel slope while $E \cdot E_{e,a1}$ and $E \cdot E_{e,a2}$, are both components of $E \cdot E_{e,a}$ the over potential. Hydrogen evolution in the anodic region could fall into the following two parts; anodic decomposition of magnesium hydride and monovalent magnesium ion oxidized by hydrogen ion [15,21]. In terms of the fundamental theory of electrochemistry, magnesium hydride decomposition in Eq. 9 depends on the magnitude of MgH₂ formed in Eq. 6. The formation of MgH₂ in Eq. 6 becomes slow as the decomposition in Eq. 9 become faster with increasing anodic potential.

$$MgH_2 \rightarrow Mg^{2+} + H_2 + 2e^{-}$$
(9)

However, the decomposition will finally cease as the equilibrium potential of magnesium hydride formation is attained. Furthermore, the contribution of magnesium hydride decomposition to NDE will be nonexistent as long as the applied potential exceeds the equilibrium potential (-0.472 V/SCE at pH 7) of Eq. 6 [10,20]. Apparently, this kind of behavior expected from fundamental theory indeed contradicts the continuous hydrogen release after the applied potential exceeds the so-called equilibrium potential of magnesium hydride formation. As a result, the continuous hydrogen release has to involve other reactions. Here, three possible reactions as shown in Eq. (10, 10a and 10b) could be expected to contribute to the NDE of Mg and its alloys. Therefore, the anodic dissolution of Mg matrix can be written as follows,

$$Mg \to Mg^+ + e^- \tag{10}$$

$$Mg^+ + H^+ \rightarrow Mg^{2+} + \frac{1}{2}H_2$$
 (10a)

$$Mg^+ \to Mg^{2+} + e^-$$
(10b)

During these processes, Mg is first transformed into Mg⁺ (Eq. 10) and then to Mg²⁺ (Eq. 10a and 10b). It is worth noting that the process from Mg⁺ to Mg²⁺ consists of two parallel reactions: (i) Mg⁺ reacts with H⁺ in a chemical reaction (Eq. 10a) [24] and, (ii) Mg⁺ is directly transformed into Mg²⁺ (Eq. 10b). The former reaction contributes to $i_{H'}$ and the latter one contributes to $i_{m'}$. Apparently, the addition of Cd does affect both $i_{m'}$ and $i_{H'}$. Fig. 9 shows that $i_{H'}$ of Mg-Cd alloy is much lower than that of pure Mg. However, $i_{m'}$ has been observed to be higher in Mg-Cd alloy. Thus, the presence of Cd in Mg-Cd alloy restrains the anodic hydrogen evolution whereas it accelerates the anodic dissolution of Mg matrix.

On SCC and microstructure:

It can be seen from the preceding sections that the addition of Cd to Mg limits the hydrogen evolution and consequently restrains the NDE in the anodic region and prevents the formation of magnesium hydride in the cathodic region. The processes lead to the lower SCC susceptibility observed in Mg-Cd alloy. One of the causes of SCC is hydrogen embrittlement, which occurs when hydrogen diffuses into the crystal structure of the metal and the dissolved hydrogen assists in the fracture of the metal. The relatively higher amount of hydrogen present on the surface of Mg makes possible hydrogen to be dissolved into the metal and be attracted to regions of high tensile stress leading to embrittlement and subsequently cracking as evidenced by the deep cracks in Fig. 6a.

Although the accelerated anodic dissolution reaction observed in Mg-Cd alloy can increase the SCC susceptibility of the alloy, the combined effect of reduced NDE, lower magnesium hydride and cathodic hydrogen formation observed in Mg-Cd alloy can contribute to reducing SCC. The sum effect of all four reactions (viz anodic dissolution, anodic hydrogen evolution, magnesium hydride formation and cathodic hydrogen evolution) results in the lower tendency of Mg-Cd alloy to undergo SCC.

4.2. Model of the effect of Cd

In order to interpret the mechanism of the effect of Cd on the corrosion behavior on Mg, we have proposed a micro-galvanic model to elucidate the effect of Cd. In the hexagonal closed-packed (hcp) Mg-Cd solution alloy, Cd as a solute atom substitutes the hcp position of the solvent Mg to form the substitutional solid solution. From the periodic table of electronegativity within the so-called Pauling scale [61], the electronegativity of Cd is 1.69 eV and the electronegativity of Mg is 1.31 eV. Therefore, we expect that Cd attracts more electrons towards itself than Mg would. The Mg-Cd alloy has an ionic form with Mg^{v+}- Cd^{δ-} galvanic couples. Moreover, the standard thermodynamics data [62] show that the equilibrium potential for $E^{\circ}_{Cd}^{2+}_{/Cd}$ is -0.402 V/SHE, whereas it is -2.372 V/SHE for $E^{\circ}_{Mg}^{2+}_{/Mg}$. At pH 7, the equilibrium potential of H⁺ reduction is -0.414 V/SHE. On basis of the experimental results, the open circuit potential of Mg-Cd alloy was detected to be -1.362 V/SHE,

which places the potential between $E_{Cd}^{\circ}^{2+}/Cd$ and $E_{Mg}^{\circ}^{2+}/Mg$. Therefore, Mg and Cd are anodically and cathodically polarized in Mg-Cd alloy respectively.

The effect of Cd in reducing the NDE, magnesium hydride formation and cathodic hydrogen evolution as well as its effect on the anodic dissolution process in Mg-Cd alloy is illustrated in Fig.12. In the cathodic process, decreasing the electrode potential can result in a more negative net charge on Cd and a less positive net charge on Mg. The electrostatic attraction of $Cd^{\delta-}$ to H⁺ will reduce the collision probability between H⁺ and Mg, and equally result in fewer H⁺ available for reduction to hydrogen. Hence, under cathodic polarization, both reactions of Eq. 5 and 6 are restrained. Furthermore, even though Cd is more negatively charged and attracts more H⁺, Cd still has a very low exchange current density for H⁺ reduction, which significantly reduces the hydrogen evolution on Cd. Therefore, the reaction of Eq. 5 is still restrained by Cd addition. In addition, since the reaction of Eq. 6 is restrained in the cathodic process, the reaction of Eq. 9 slows down accordingly in the anodic process. These reactions can partially reduce the NDE of magnesium.



Figure 12. Illustrations of the Mg^{v+}- Cd^{δ-} galvanic couples charged in the anodic, open circuit potential and cathodic regions. Longer arrows represent greater attraction or greater repulsion of charges while shorter arrows represent lesser attraction or lesser repulsion of charges. The directions of the arrows reflect either attraction or repulsion.

In the anodic process of Mg-Cd alloy, increasing the electrode potential results in a less negative net charge on Cd and a more positive net charge on Mg. This process accelerates the anodic reactions (Eq. 10 and 10b) but prevents the reaction of Eq. 10a. The reason for the accelerated anodic reactions is mainly due to the static Coulombs attraction effect within the Mg^{v+}- Cd^{δ -} galvanic couple, which results in a more positively charged Mg in Mg-Cd alloy with respect to pure Mg at the same potential. As expected, it induces an easier reaction (Eq. 10b) for Mg-Cd than for pure Mg. In the meanwhile, the collision probability of the reaction in Eq. 10a is significantly reduced due to the stronger electrostatic repulsion between Mg^{v+} and H⁺ in Mg-Cd alloy. In addition, Cd with a few net

negative charges exhibits an ability to attract H^+ by a weak electrostatic attraction. This process results in a decrease in the collision probability between Mg^+ and H^+ as well. Therefore, the addition of Cd to Mg matrix effectively reduces the anodic hydrogen evolution rate and, consequently, reduces the NDE.

5. CONCLUSIONS

In summary, we have investigated the improvement of the corrosion-resistant behavior and the mechanical performance of Mg by alloying with Cd. Investigations were carried out on pure Mg and Mg-Cd alloy by gas collection, electrochemical measurements, DSC and tensile stress tests. The results highlight the suitability of alloying Cd (2 wt.%) to Mg in improving its corrosion resistant performance and its SCC resistance . The addition of Cd to Mg restrained the cathodic hydrogen evolution, MgH₂ formation and NDE and accelerated the anodic dissolution of Mg in Mg-Cd alloy. The reduction in MgH₂ formation was confirmed by a lower MgH₂ decomposition amount in the Mg-Cd alloy. Furthermore, we have provided an understanding to the corrosion mechanisms occurring in the alloy in terms of its chemistry using an Mg^{v+}- Cd^{δ -} micro-galvanic couple model. This model presents itself a useful tool in the interpretation of the corrosion mechanisms in Mg alloys.

ACKNOWLEDGEMENTS

This work has been funded by the National Basic Research Program of China (grant number: 2007CB613705) and the National Natural Science Foundation of China (Grant number: 50971120). The authors gratefully acknowledge Dr. Jie Wang who provided the Mg-Cd alloy. The first author also wishes to thank Prof. Xingqiu Chen and Dr. Magdalene Edet Ikpi for the modifications to the paper. M. E. Ikpi acknowledges the Chinese Academy of Sciences (CAS) and the Academy of Sciences for the Developing World (TWAS), for the CAS-TWAS Postdoctoral Fellowship.

References

- 1. I. J. Polmer, Mater. Sci. Technol., 10 (1994) 1
- 2. A. Luo, M. O. Pekguleryuz, J. Mater. Sci., 29 (1994) 5259
- 3. F. H. Froes, D. Eliezer, E. Aghion, JOM, 50 (1998) 30
- 4. J. W. Chang, X. W. Guo, P. H. Fu, L. M. Peng, W. J. Ding, Electrochim. Acta, 52 (2007) 3160
- 5. X. B. Liu, D. Y. Shan, Y. W. Song, R. S. Chen, E. H. Han, *Electrochim. Acta*, 56 (2011) 2582
- 6. A. E. Coy, F. Viejo, P. Skeldon, G. E. Thompson, Corros. Sci., 52 (2010) 3896
- 7. Y. W. Song, D. Yong, Y. Shan, R. S. Chen, E. H. Han, Corros. Sci., 52 (2010) 1830
- 8. M. Liu, P. Schmutz, P. J. Uggowitzer, G. Song, A. Atrens, Corros. Sci., 52 (2010) 3687
- 9. A. Atrens, Adv. Eng. Mater., 6 (2004) 83
- 10. G. L. Song, A. Atrens, Adv. Eng. Mater., 1 (1999) 11
- 11. G. Song, A. Atrens, Adv. Eng. Mater., 5 (2003) 837
- 12. J. X. Jia, A. Atrens, G. Song, T. H. Muster, Mater. Corros., 56 (2005) 468
- 13. J. X. Jia, G. Song, A. Atrens, Corros. Sci., 48 (2006) 2133
- 14. N. Winzer, A. Atrens, G. Song, E. Ghali, W. Dietzel, K. U. Kainer, N. Hort, C. Blawert, Adv. Eng. Mater., 7 (2005) 659
- 15. F. Guadarrama-Munoz, J. Mendoza-Flores, R. Duran-Romero, J. Genesca, Electrochim. Acta, 51

(2006) 1820

- 16. G. Song, A. Atrens, D. St John, J. Nairn, Y. Li, Corros. Sci., 39 (1997) 855
- 17. G. Song, A. Atrens, D. St John, X. Wu, J. Nairn, Corros. Sci., 39 (1997) 1981
- 18. G. Song, A. Atrens, M. Dargusch, Corros. Sci., 41 (1999) 249
- 19. W. J. James, M. E. Straumanis, B. K. Bhatia, J. W. Johnson, J. Electrochem. Soc., 110 (1963) 1117
- 20. J. Chen, J. H. Dong, J. Q. Wang, E. H. Han, W. Ke, Corros. Sci., 50 (2008) 3610
- 21. R. L. Petty, A. W. Davidson, J. Kleinberg, J. Am. Chem. Soc., 76 (1954) 363
- 22. E. Gulbrandsen, *Electrochim. Acta*, 37 (1992) 1403
- 23. A. Nazarov, A. Lisovskii, Y. Michailovskii, Zashch. Met., 25 (1989) 760
- 24. E. Gulbrandsen, J. Taftø, A. Olsen, Corros. Sci., 34 (1993) 1423
- 25. C. H. Brun, J. Pagetti, J. Talbot, Mem. Sci. Rev. Metall., 73 (1976) 659
- 26. J. Chen, J. Q. Wang, E. H. Han, J. H. Dong, W. Ke, Corros. Sci., 50 (2008) 1292
- 27. A. Seyeux, M. Liu, P. Schmutz, G. Song, A. Atrens, P. Marcus, Corros. Sci., 51 (2009) 1883
- 28. G. G. Perrault, J. Electroanal. Chem., 51 (1974) 107
- 29. J. Chen, J. Q. Wang, E. H. Han, W. Ke, Mater. Sci. Eng. A., 488 (2008) 428
- 30. R. S. Stampella, R. P. M. Procter, V. Ashworth, Corros. Sci., 24 (1984) 325
- 31. R. G. Song, C. Blawert, W. Dietzel, A. Atrens, Mater. Sci. Eng. A., 399 (2005) 308
- 32. Y. Zhang, X. Zhou, Z. Wei, Y. Huang, Mater. Sci. Forum, 650 (2010) 272
- 33. A. Atrens, W. Dietzel, Adv. Eng. Mater., 9 (2007) 292
- 34. J. Swiatowska, P. Volovitch, K. Ogle, Corros. Sci., 52 (2010) 2372
- 35. G. Williams, H. N. McMurray, J. Electrochem. Soc., 155 (2008) 340
- 36. S. Bender, J. Goellner, A. Heyn, S. Schmigalla, Mater. Corros., 62 (2011) 1
- 37. R. W. Revie, H. H. Uhlig, Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering, John Wiley & Sons Inc., Hoboken, New Jersey (2008)
- 38. H. Kita, J. Electrochem. Soc., 113 (1966) 1095
- 39. D. B. Mahler, L. G. Terkla, J. V. Eysden, M. H. Reisbick, J. Dent. Res., 49 (1970) 1452
- 40. R. Castanet, Z. Moser, W. Gasior, Calphad., 4 (1980) 231
- 41. D. Hardie, R. Parkins, Philos. Mag., 4 (1959) 815
- 42. F. Batchelder, R. Raeuchle, Phys. Rev., 105 (1957) 59
- 43. M. M. Avedesian, H. Baker, Eds., *ASM Specialty Handbook, Magnesium and Magnesium Alloys*, ASM international-The Materials Information Society, Ohio (1999)
- 44. E. M. Savitsky, *The influence of temperature on the mechanical properties of metals and alloys*, Stanford University Press, California (1961)
- 45. N. N. Gratsianskii, P. E. Kaluzhnaya, Zh. Fiz. Khim., 32 (1958) 1038
- 46. G. Song, A. Atrens, D. H. St. John, In An hydrogen evolution method for the estimation of the corrosion rate of magnesium alloys, J. N. Hyrn, Ed., Magnesium Technology 2001 Symposium; Minerals, Metals & Material Society: New Orleans, LA (2001)
- 47. D. A. Jones, *Principles and Prevention of Corrosion*, 2nd Ed., Prentice Hall, Upper Saddle River, New Jersey (1996)
- 48. M. C. Zhao, M. Liu, G. Song, A. Atrens, Adv. Eng. Mater., 10 (2008) 104
- 49. T. Zhang, Y. W. Shao, G. Z. Meng, Y. Li, F. H. Wang, Electrochim. Acta, 52 (2006) 1323
- 50. Powder Diffraction File, International Centre for Diffraction Data: PDF#89-4244.
- 51. N. N. Aung, W. Zhou, Corros. Sci., 52 (2010) 589
- 52. J. Chen, J. Q. Wang, J. H. Dong, E. H. Han, W. Ke, Mater. Corros., 57 (2006) 789
- 53. S. N. Xu, J. H. Dong, W. Ke, Inter. J. Corros., 2010 (2010) 1
- 54. J. H. Dong, S. N. Xu, W. Ke, N. Chen, Mater. Sci. Forum, 654-656 (2010) 779
- 55. K. B. Gerasimov, E. Y. Ivanov, Mater. Lett., 13 (1985) 497
- 56. D. Fátay, A. Révész, T. J. Spassov, Alloys Compd., 399 (2005) 237
- 57. E. I. Meletis, R. F. Hochman, Corros., 40 (1984) 39
- 58. M. B. Kannan, W. Dietzel, R. K. R. Singh, L. Paul, Scr. Mater., 57 (2007) 579

- 59. S. P. Lynch, Mechanisms of Hydrogen Assisted Cracking A Review. In Hydrogen Effects on Material Behavior and Corrosion Deformation Interactions, N. R. Moody, A. W. Thompson, R. E. Ricker, G. W. Was, R. H. Jones, Eds., TMS, Warrendale, PA (2003)
- 60. G. Liang, R. Schulz, J. Mater. Sci., 39 (2004) 1557
- 61. R. S. Evans, J. E. Huheey, J. Inorg. Nucl. Chem., 32 (1970) 373
- 62. M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, NACE International, Houston (1974)

© 2012 by ESG (www.electrochemsci.org)