

CORROSION PERFORMANCE OF Mg-Ti ALLOYS SYNTHESIZED BY MAGNETRON SPUTTERING

Zhenqing Xu¹, Guang-Ling Song^{2*}, Daad Haddad¹

¹MEDA Engineering and Technical Services, LLC, 17515 W 9 Mile Rd, STE 1075, Southfield, MI 48075, USA

²General Motors Research and Development, Mail Code: 480-106-224, 30500 Mound Road, Warren, MI 48090, USA

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Abstract

Mg is difficult to alloy with Ti through a conventional metallurgical approach due to their insolubility in each other and big difference in melting point. However, Mg, if alloyed with Ti, may become corrosion resistant. This hypothesis is verified in this study.

Mg_{1-x}Ti_x alloy thin films (with x=0, 0.2, 0.4, 0.6, 0.8 and 1) were deposited by magnetron sputtering onto a glass substrate. Film compositions were analyzed by electron probe micro-analysis (EPMA). The electrochemical behavior of these alloys was characterized in saturated Mg(OH)₂ solutions with and without 0.1M NaCl. The macrostructures of the thin film alloys were compared before and after polarization and immersion measurements. The results showed that the corrosion resistance of the alloy was improved with increasing Ti content. No material loss or corrosion damage was observed for alloys with 80% or more Ti content in both solutions.

Introduction

Mg alloys have found many potential applications recently. Their low density and high strength to weight ratio make Mg alloys attractive to the auto industry in weight reduction and efficiency improvement. However, many of the alloying elements form intermetallic phases with Mg which have a more positive free corrosion potential than the Mg matrix itself [1-3]. Hence, micro-galvanic corrosion attacks usually decrease the overall corrosion resistance of a Mg alloy. It is hypothesized that a precipitation free, single phase, solid solution magnesium alloy will have better corrosion performance.

Mg and Mg alloys present a very negative open circuit potential in a sodium chloride solution and have an active and fast anodic dissolution process [4]. The addition of strong passivation elements like Cr [5] and Ti [6-8] could possibly improve the passivity of a Mg alloy. However, according to the phase diagram, the solubility of Mg in Ti, and vice versa, is very small in crystalline state. Conventional equilibrium metallurgical approach cannot successfully lead to a Mg-Ti solid solution phase due to low solid solubility in each other and very high Ti melting point relative to Mg. Using a non-equilibrium magnetron sputtering deposition technique can substantially extend the solubility of Ti in the Mg-Ti alloy and in this case the large melting point difference between Ti and Mg is no longer an issue.

In this paper, Mg-Ti thin film alloys with different Ti concentrations were deposited and their corrosion behavior was compared, aiming to understand the effect of the Ti solute on the corrosion behavior of Mg.

Experimental

Film Deposition

Mg_{1-x}Ti_x (x=0, 0.2, 0.4, 0.6, 0.8, 1) thin films were deposited onto a round glass disk, 2 cm in diameter, using dc magnetron sputtering in an argon atmosphere at room temperature. The base pressure in the growth chamber was about 5×10⁻⁸ Torr. The dynamic pressure during film deposition was 2 mTorr. High purity Mg and Ti ingots were used as targets. The thin film was very uniformly formed on the glass substrate. Film composition was controlled by changing the power applied to the Mg and Ti targets. The compositions of the different Mg-Ti thin film samples were confirmed by Electron Probe Microanalysis (EPMA).

Electrochemical Characterization

A glass flat cell and a Solatron 1280 potentiostat system were used for polarization curve measurements. The sample was immersed in the solution at its open circuit potential (OCP) for 5 min before polarization curve measurement. The immersed area was 1 cm². A platinum gauze (2.5 cm x 2.5 cm) was used as the counter electrode and a KCl-saturated Ag/AgCl electrode was used as the reference (Ref). Potentiodynamic polarization curve was recorded at a potential scanning rate of 0.1 mV/s from -0.2 V vs. OCP to +1.0 V vs. Ref.

Immersion Test and Surface Film Characterization

Mg-Ti thin film samples were immersed in Mg(OH)₂+0.1M NaCl solution for 4 days. Their morphologies after immersion were examined under optical microscope and Scanning Electron Microscope (SEM). A small section in the immersion area was analyzed by X-ray photoelectron spectroscopy (XPS). High resolution XPS has also been performed on Mg 2p, O 1s, and Ti 2p core levels. As is the standard practice in XPS studies, the C1s line corresponding to the C-C bond has been used as the binding energy (BE) reference [9].

Results and Discussion

Deposition and Film Composition

The deposition conditions for growing Mg-Ti thin films and the EPMA composition characterization are listed in Table I. By changing the power applied to the Mg and Ti targets, different growth rates of Mg and Ti can be achieved, forming Mg-Ti thin films with different Ti contents. The EPMA measurements confirm that the deposition parameters used in sputtering quite accurately controlled the thin film compositions. Thickness of these thin films has been measured by cross section SEM. These samples have thickness ranging from 1.2 μm to 1.5 μm.

Table I. EPMA composition characterization of Mg-Ti thin films deposited by magnetron sputtering

Sample	Power (W)		Rate (Å/s)		Calculated Concentration (Using Growth rates)%at		Measured Concentration (EPMA)%at		Measured Thickness (Cross section SEM) μm
	Mg	Ti	Mg	Ti	Mg	Ti	Mg	Ti	
Mg	100	-	4.6	-	100	-	>99	<1	1.2
Mg80Ti20	100	130	4.6	0.9	80	20	79	21	1.3
Mg60Ti40	50	200	2.5	1.3	60	40	59	41	1.3
Mg40Ti60	40	310	2.0	2.1	40	60	42	58	1.5
Mg20Ti80	20	450	1.0	2.9	20	80	19	81	1.4
Ti	-	300	-	2.0	-	100	<1	>99	1.3

Corrosion Behavior

To investigate the effect of Ti on Mg-Ti alloy's electrochemical behavior, potential-dynamic polarization curves were measured in Mg(OH)₂ solutions, with and without 0.1M NaCl. Polarization curves of sputter-deposited pure Mg and Ti were also measured for comparison.

Figure 1 shows macroscopic images of the Mg-Ti alloys after polarization in both solutions. The top part of the coupon sample has undergone the polarization measurements in the Mg(OH)₂ saturated solution, while the bottom part is in the solution with 0.1M sodium chloride addition. For samples polarized in saturated Mg(OH)₂, significant material loss can be observed for pure Mg, Mg80Ti20 and Mg60Ti40. Particularly for pure Mg, no material was preserved after polarization to +1 V vs. Ref. Obviously, a film with increased Ti content was less corroded, indicating that a increase in Ti content can lead to improved corrosion resistance.

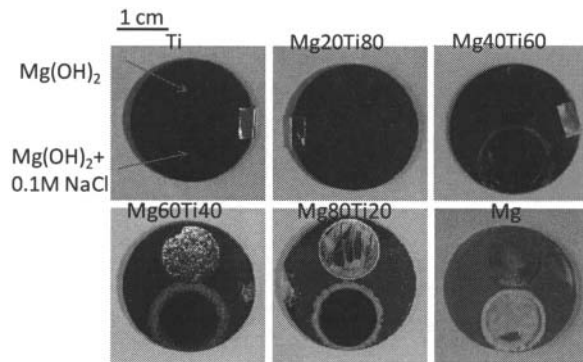


Figure 1. Macroscopic images of Mg-Ti thin films on glass disks after polarization in saturated Mg(OH)₂ (top round areas) and Mg(OH)₂+0.1 M NaCl (bottom round areas).

With the addition of 0.1M sodium chloride, similar behaviors of these films were observed. Apparent corrosion can be found for all samples other than pure Ti and Mg20Ti80, although much of the materials were preserved for Mg40Ti60, Mg60Ti40 and

Mg80Ti20. Crevice corrosion was found at the areas that were in contact with the plastic washer of the electrolyte cell. The severity of the crevice corrosion is in reverse order of the Ti content in the Mg-Ti alloys. The above macroscopic observations show that with increased Ti content, a Mg-Ti alloy thin film becomes more resistant to general corrosion during polarization. Their ability to preserve more material when being anodized with high overvoltage has increased significantly. It is widely known that the corrosion of Ti results in a stable oxide layer (essentially TiO₂) on the surface. The improved passivity of a Mg-Ti alloy with increasing Ti content could result from formation of more TiO₂ on the surface.

Figure 2 shows the polarization curves of Mg-Ti alloys measured in saturated Mg(OH)₂ without (a) and with (b) 0.1M NaCl. The influence of the noble Ti on the free corrosion potential can be clearly identified. The higher the Ti content, the more positive is the corrosion potential.

In Mg(OH)₂ solution shown in Figure 2a, very little passive tendency is observed for Mg and Mg80Ti20. As the polarization potential is more positive than +0.5 V vs. Ref the current density decreases significantly. This phenomenon cannot be linked to passivation of the material. Rather, considering the previous observation from Figure 1, we can conclude that at a voltage more positive than +0.5 V vs. Ref, significant material was corroded for these two samples and the inert substrate glass was exposed to the solution, resulting in decreased anodic dissolution current densities.

A clear passive regime with constant current can be seen in the anodic region for samples with Ti content larger than 40%. Although Mg60Ti40 has the lowest passivation current density, it loses its passivation when potential is more positive than 0.25 V vs. Ref. Other than Mg60Ti40, the passivation current densities decrease with more Ti addition into Mg-Ti for Mg-Ti alloy when Ti content is higher than 60at%. This higher corrosion resistance can be attributed to structure modification of Mg film by substitution of Mg with Ti and improved stability of the surface film due to Ti incorporation.

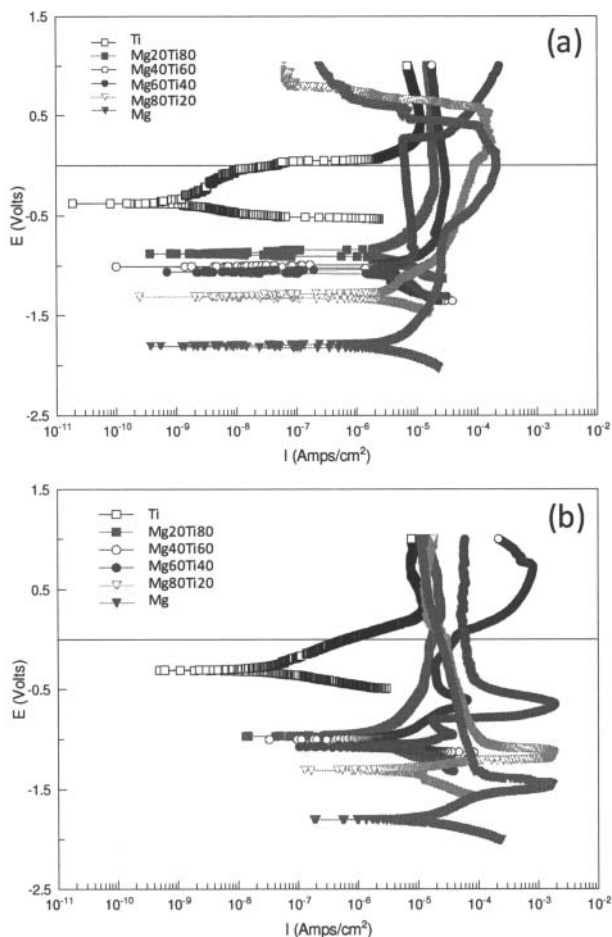


Figure 2. Polarization curves of Mg-Ti thin films in (a) in saturated $Mg(OH)_2$ and (b) saturated $Mg(OH)_2+0.1 M NaCl$;

Similar electrochemical behavior has been observed in solution of $Mg(OH)_2+0.1M NaCl$ (Figure 2b). Because of the presence of corrosive Cl^- in the solution, no passivity can be detected for pure Mg and $Mg_{80}Ti_{20}$. Both $Mg_{60}Ti_{40}$ and $Mg_{40}Ti_{60}$ have a small passive region while the latter one has a higher passivation potential and a broader passive potential region from -0.6 to -0.2 V vs. Ref. A dramatic anodic dissolution current density decrease was recorded for Mg-Ti thin films with Ti content less than 40%. A possible scenario is that most of the material was corroded at the crevice corrosion region (shown as a corroded ring in Figure 1) and became electrically insulating, leading to a diminished current density shown in Figure 2b. $Mg_{20}Ti_{80}$ and pure Ti stay in the passive region even when the polarization potential is at +1 V vs. Ref.

Immersion Test

Mg-Ti thin films morphologies were recorded using an optical microscope for different immersion times in the saturated $Mg(OH)_2+0.1M NaCl$ solution (Figure 3). The top part of each image is where the sample was immersed. It was found that after 1 hour of immersion pure Mg was corroded significantly with pitting and cracking evident all over the immersed area. No

material loss or cracking can be observed for $Mg_{80}Ti_{20}$; only a slight color change is found. It was previously shown in Figure 2 that under polarization $Mg_{60}Ti_{40}$ was more corrosion resistant than $Mg_{80}Ti_{20}$. However, an interesting finding is that after 1 hour immersion $Mg_{60}Ti_{40}$ experienced more material loss from the substrate than $Mg_{80}Ti_{20}$. For Mg-Ti alloys with over 40 at.%Ti, no corrosion occurred on their surface after immersion.

After 4 hour immersion (Figure 3b), all Mg was corroded away for pure Mg thin film. There is no significant material loss for $Mg_{80}Ti_{20}$. A gap between the top and bottom parts is found, suggesting that some of the film was dissolved along the waterline. $Mg_{60}Ti_{40}$ has lost considerable amount of the film after 4 hours of immersion. No corrosion can be detected on all other samples.

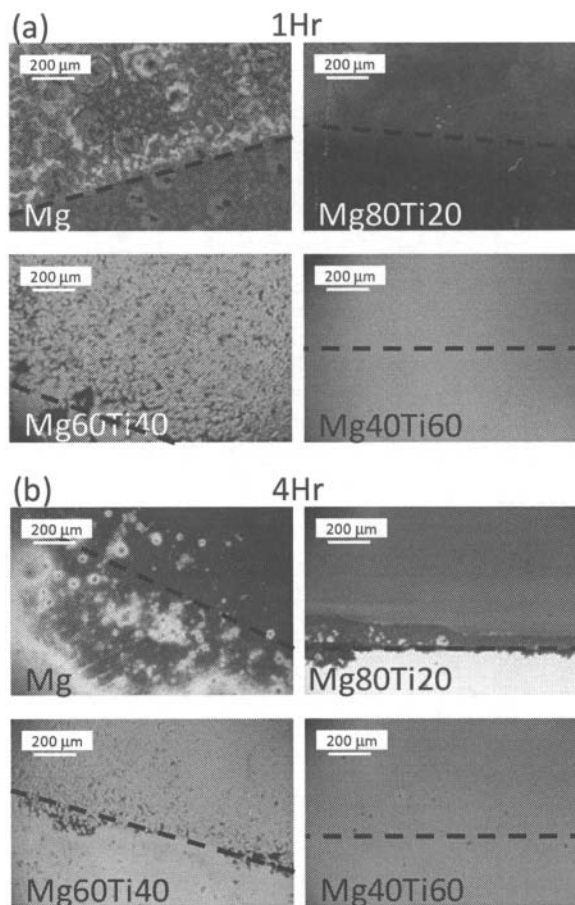


Figure 3. Macroscopic images of Ti-Mg thin film alloys after immersion in $Mg(OH)_2+0.1M NaCl$ for (a) 1hr and (b) 4 hr. The top part of the graph is the immersed area.

Further analysis of the structure of these Mg-Ti thin films after immersion test is presented by SEM in Figure 4. Under high magnification cracks can be found in $Mg_{80}Ti_{20}$, $Mg_{60}Ti_{40}$ and $Mg_{40}Ti_{60}$ samples after 4 hour immersion. It seems that the most severe film rupture and cracking is found in $Mg_{60}Ti_{40}$ (Figure 4b). The density of micro-cracks in $Mg_{80}Ti_{20}$ is the highest; however, the film seems to adhere very well to the glass substrate. There is no film peeling or delamination. The SEM observation

confirms the previous macroscopic finding that Mg60Ti40 has more material loss than Mg80Ti20 after 4 hours of immersion test. Although polarization results suggest that Mg60Ti40 shows more passive nature than Mg80Ti20 (Figure 2), more concentrated stress presented in the film could lead to peeling and delamination after the sample is taken out from the solution and exposed to air. Further analysis such as X-ray diffraction (XRD) and atomic force microscopy (AFM) are being conducted to investigate why stress is more uniformly presented in Mg80Ti20. The grain size, orientation or mechanical properties of the Mg-Ti thin films may all play a role in the stress distribution. Moreover, the difference in strength and brittleness of the compounds could also result in different film cracking patterns.

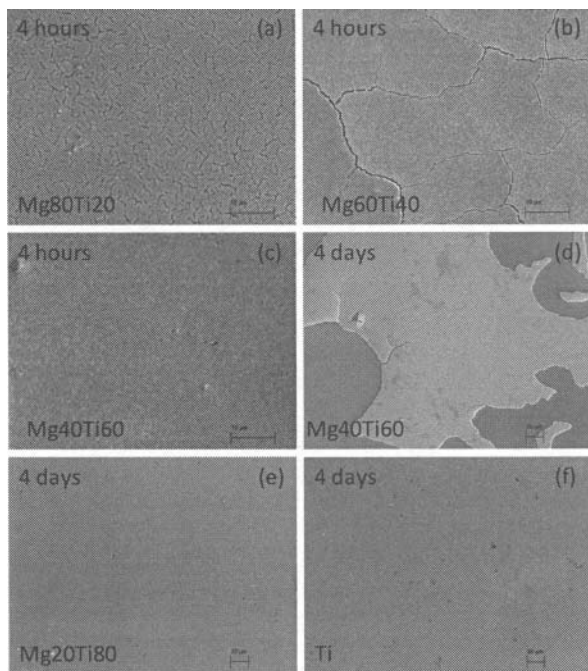


Figure 4. SEM micrographs of Ti-Mg thin film alloys after immersion in $\text{Mg}(\text{OH})_2+0.1 \text{ M NaCl}$.

Immersion test was continued for 4 days for Mg40Ti60, Mg20Ti80 and pure Ti. There is still no cracking or material loss observed for pure Ti and Mg20Ti80 (Figure 4e and f). A small amount of Mg40Ti60 was still left on the substrate (Figure 4d) while Mg80Ti20 and Mg60Ti20 have lost all of the deposited films. Overall, the improvement of corrosion resistance is evident when the Ti content is increased. This beneficial effect observed for Mg-Ti alloys could be partially attributed to the excellent corrosion resistance of Ti. Corrosion of Mg occurs at breaks in a partially protected surface film. The passive film $\text{Mg}(\text{OH})_2$ is mechanically weak and unstable and not able to prevent further corrosion of Mg. The formation of continuous TiO_2 passive layer should play an important role in increasing the corrosion resistance of Mg-Ti alloys.

XPS Characterization

XPS measurement was conducted on two selected samples, Mg20Ti80 and Mg80Ti20 after 4 hour immersion test. The survey

spectra revealed the presence of Mg 2p, O 1s and Ti 2p. These characteristic peaks correspond to the electron configuration of the electrons within the atoms. High resolution Mg 2p XPS spectra (Figure 5a) show that one broad peak at 50.8 eV is presented for both specimens, suggesting the existence of MgO and $\text{Mg}(\text{OH})_2$. The O 1s spectra presented in Figure 5b show different characteristics for these two samples. The Mg20Ti80 sample has only one main O 1s peak presented at 531.0 eV, corresponding to oxide. The O 1s composite peak of Mg80Ti20 sample can be deconvoluted to two big peaks, corresponding to oxide (531.0 eV) and hydroxide (532.8 eV). The measured high resolution peaks for Ti 2p are shown in Figure 5c. The peak positions 459.0 for Ti oxide is in very good agreement with the literature values given for TiO_2 (458.7 eV) [7].

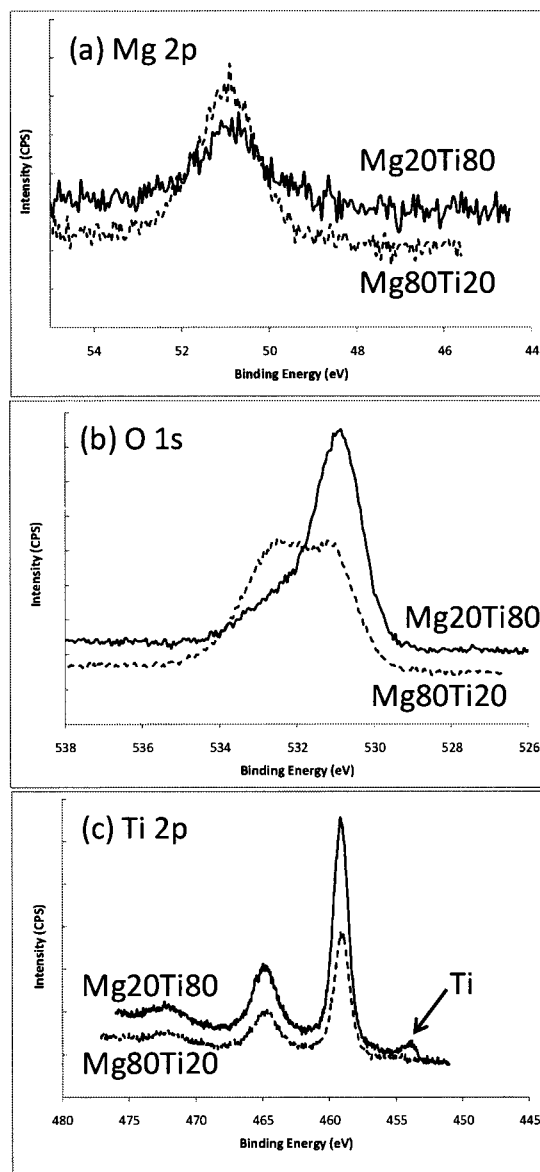


Figure 5. XPS high resolution spectra of Ti-Mg after immersion in $\text{Mg}(\text{OH})_2+0.1 \text{ M NaCl}$.

The above findings suggest that the Mg₂₀Ti₈₀ sample surface has a strong oxide layer, possibly TiO₂. It confirms our previous speculation that a stable oxide layer could form on the alloy with higher Ti content and prevent corrosion attack. A small peak is also presented for Mg₂₀Ti₈₀ sample at 453.0, corresponding to Ti in its metallic state. For the Mg₈₀Ti₂₀ sample, Mg is not only presented in its oxide state, but also in the surface film Mg(OH)₂. Unfortunately, this film is not very protective [10, 11]. Only a higher concentration of Ti in the film can beneficially enhance the passivity. The mixture of TiO₂ and MgO forms a compact passive film preventing the attack of aggressive Cl⁻ ions, leading to improved corrosion resistance of a Mg-Ti alloy with a higher Ti content.

Summary

The corrosion properties of Mg_xTi_{1-x} thin films with x ranging from 0 to 1 were investigated. Incorporation Ti in the Mg lattice has been achieved by dc magnetron sputtering. Polarization measurements showed that alloys with high Ti content had better passivity in solutions of Mg(OH)₂ with and without 0.1M NaCl. XPS observation confirms the presence of surface oxide film on the Mg-Ti alloy surface. A high ratio of oxide/hydroxide in the Mg₂₀Ti₈₀ sample surface is responsible for improved corrosion resistance.

Production of supersaturated single-phase compounds of Mg-Ti coatings by sputtering provides a promising approach to produce corrosion resistance magnesium based alloys outside the conventional casting technology. Formation of precipitates during sputtering is strongly reduced. As a result, high purity coatings can be obtained and a reduced corrosion rate can be achieved. Compound composition strongly influences the properties and corrosion behaviors of the alloy films. Therefore, other corrosion resistant materials could also be used to form alloys with Mg to prevent corrosion.

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