Corrosion resistance and cytocompatibility of biodegradable surgical magnesium alloy coated with hydrogenated amorphous silicon

Yunchang Xin,¹,² Jiang Jiang,¹ Kaifu Huo,¹ Guoyi Tang,² Xiubo Tian,³ Paul K. Chu¹
¹Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China
²Advanced Materials Institute, Tsinghua University, Shenzhen graduate school, Shenzhen 518055, China
³State Key Laboratory of Welding Production Technology, School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

Received 29 October 2007; revised 26 January 2008; accepted 7 February 2008
Published online 30 April 2008 in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/jbm.a.32006

Abstract: The fast degradation rates in the physiological environment constitute the main limitation for the applications of surgical magnesium alloys as biodegradable hard-tissue implants. In this work, a stable and dense hydrogenated amorphous silicon coating (a-Si:H) with desirable bioactivity is deposited on AZ91 magnesium alloy using magnetron sputtering deposition. Raman spectroscopy and Fourier transform infrared spectroscopy reveal that the coating is mainly composed of hydrogenated amorphous silicon. The hardness of the coated alloy is enhanced significantly and the coating is quite hydrophilic as well. Potentiodynamic polarization results show that the corrosion resistance of the coated alloy is enhanced dramatically. In addition, the deterioration process of the coating in simulated body fluids is systematically investigated by open circuit potential evolution and electrochemical impedance spectroscopy. The cytocompatibility of the coated Mg is evaluated for the first time using hFOB1.19 cells and favorable biocompatibility is observed. © 2008 Wiley Periodicals, Inc. J Biomed Mater Res 89A: 717–726, 2009

Key words: magnesium alloy; hydrogenated amorphous silicon coating; corrosion resistance; cytocompatibility

INTRODUCTION

Magnesium-based alloys are potential materials in biodegradable hard-tissue implants and good biocompatibility has been observed in clinical samples and in vivo and in vitro assessments.¹–³ Some studies have also shown that the dissolved magnesium ions may promote bone cell attachment and tissue growth on the implants.⁴–⁶ Unfortunately, pure magnesium and its alloys corrode too quickly at the physiological pH (7.4–7.2) as well as in physiological media containing high concentrations of chloride ions, thereby losing mechanical integrity before tissues have sufficient time to heal.¹,³,⁷,⁸

Various methods have been developed to improve the corrosion resistance of Mg alloys and examples are alkali-heat treatment,⁹ plasma immersion ion implantation,¹⁰ microarc oxidation,¹¹ and so on. One of the most effective ways to protect materials from the corrosive media is to coat the base materials. The coating must, however, be uniform, well-adhesive, free of pores, and corrosion-resistant. In biomedical applications, the coatings must also possess both good biocompatibility and desirable bioactivity. In the past three decades, silicon has gradually been recognized to be an essential trace element in the normal metabolism of higher animals. Studies have demonstrated that silicon is involved in bone, cartilage, and connective tissue formation as well as several other important metabolic processes.¹² Hidebrant et al.¹³,¹⁴ have used modern genetic engineering techniques to demonstrate that certain genes are activated by hydrated silicon. Hydrated soluble silicon has been shown to enhance the proliferation of bone cells (osteoblasts) and active cellular production of transforming growth factors.¹³,¹⁴ Hydrogenated amorphous silicon (a-Si:H) possesses unique electrical and optical properties and is used in optical-electronic devices such as solar cells, color sensors, and thin-film transistors.¹⁵–¹⁷ However, its
applications as a substrate or functional materials in the biological and medical fields are still in the infancy. Dahmen et al.\textsuperscript{18} have shown that hydrogenated amorphous silicon and amorphous silicon suboxide films are largely biocompatible after hydrolylation reactions. Liu et al.\textsuperscript{19} have also found that hydrogenated amorphous films can induce precipitation of apatite. Chemical vapor deposition, plasma-enhanced chemical vapor deposition, and magnetron sputtering deposition are often used to produce uniform, high-quality, and large area a-Si:H films at high deposition rates.\textsuperscript{16} Thus, further development of silicon-based materials is promising in the biomaterial field.

In the work reported here, a-Si:H coatings are deposited on die-cast AZ91 magnesium alloy by direct current magnetron sputtering deposition. The a-Si:H coating with good adhesion not only serves as a barrier to isolate the substrate from extensive corrosion, but also can provide a bioactive surface. The structure of the coating and electrochemical behavior of the coated alloy are systematically investigated. In addition, the cytocompatibility of the materials is determined for the first time by means of cell culture experiments.

**EXPERIMENTAL DETAILS**

**Sample preparation**

Die-cast AZ91 magnesium alloy rods were cut into 15 × 15 × 5 mm\textsuperscript{3} and 10 × 10 × 2 mm\textsuperscript{3} blocks. The samples were ground with No. 4000 water proof grinding paper, polished, and then ultrasonically cleaned in alcohol. According to the literature, a sample temperature range of 200–300°C favors the formation of monohydride a-Si:H films and a working gas pressure in the range 1–4 Pa gives rise to denser films.\textsuperscript{20,21} Therefore, in our experiments, the substrate temperature was maintained at about 210°C and the pressure of 1.5 Pa. A mixture of Ar and H\textsubscript{2} (flow ratio of 6:1) was used and the deposition time was 1 h. The treated and untreated samples were designated as “as-coated” and “as-cast,” respectively in our experiments and analysis.

**Characterization**

Raman spectra were acquired from the hydrogenated amorphous silicon-coated Mg in the backscattering mode using a DILLORyISA LabRAM 010 system equipped with an unpolarized HeNe laser. The excitation line wavelength was 632.8 nm, and the laser power was 6.4 mW. Fourier transform infrared (FTIR) spectroscopy was utilized to identify the functional groups in the coating. Both pan views and cross-sectional views of the coating were obtained by scanning electron microscopy (SEM, HITACHI S-4700). Before obtaining the cross-sectional micrographs, the sample was mounted by resin and then gold-coated. Energy dispersive X-ray (EDS) line scans were performed across the interface between the coating and substrate to determine the distribution of magnesium and silicon across the region.

**Vickers hardness and water contact angle measurements**

The hardness of both the substrate and coating were measured on a Vickers Hardness tester (Digital Microhardness tester, HVS-1000) under a load of 5 g and loading time of 20 s. The sessile water contact angle was obtained on a Ramé-hart contact angle instrument at room temperature. Fifty microliters of deionized water was placed on the surface of each sample, and the image of the water droplet was captured by a video camera. The water contact angle was measured and calculated by the Dropimage Standard software. The measurement was repeated four times to obtain good statistics.

**Electrochemical test**

The electrochemical behavior of both the treated and untreated samples in simulated body fluids (SBF) was studied by potentiodynamic polarization test, open circuit potential evaluation (Ecorr - t), and electrochemical impedance spectroscopy (EIS) using Gamry Reference 600. The ion concentrations in SBF are shown in Table I.\textsuperscript{22} A three-electrode cell system comprising the sample as the working electrode, saturated potassium chloride electrode as the reference electrode, and platinum sheet as the counter electrode was employed in this study. In the potentiodynamic polarization test, a scanning rate of 2 mV s\textsuperscript{-1} was applied. As magnesium corroded quickly in the SBF, the test of the untreated alloy commenced immediately after it was dipped into the solution. For the coated alloy, scanning began after it was soaked in the solution for 30 min. The open circuit potential evolution of the sample was monitored as a function of immersion time for 100 ks. The potential was recorded very 15 s. The impedance data were recorded at open circuit potential from 100 kHz to 10 mHz with a 10 mV root mean square (rms) amplitude sinusoidal perturbing signal. The lowest frequency was set to 10 mHz in order to reduce the time and potential noise.

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>Ion Concentrations in Simulated Body Fluids (SBF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mmol/L)</td>
<td>Na\textsuperscript{+}</td>
</tr>
<tr>
<td>SBF</td>
<td>142.0</td>
</tr>
<tr>
<td>Blood plasma</td>
<td>142.0</td>
</tr>
</tbody>
</table>

*Journal of Biomedical Materials Research Part A*
interference. The EIS measurement was affected by phase shift from potentiostat in the high-frequency region, and so the upper limit was set to 100 kHz. In the EIS measurement, after the sample was soaked in the solution, the sample stayed in the solution until the final test was completed. With regard to the analysis of the impedance data, the appropriate equivalent circuit (EC) that not only matched the physical structure of measured electrode system but also was able to produce similar spectra was adopted. The values of the relevant components were fitted using the ZsimpWin software. All the electrochemical tests were performed at room temperature.

**Cell cultures**

The cytocompatibility of the coated alloy was assessed by cell culture experiments using hFOB 1.19 cells. The samples before the cell experiments were coated on both sides. The cells were cultured in a complete medium consisting of a mixture of 45% Dulbecco’s modified eagle medium (Invitrogen Cat no. 11995-040), 45% F-12 (Invitrogen Cat no. 11765-047), and 10% fetal calf serum (HyClone Cat no. SV30087.02). The cell cultures were maintained at 34°C under 95% air and 5% CO₂. The subconfluent monolayers were dissociated with a 0.01% solution of trypsin and resuspended into a fresh complete medium. A 100 μL complete culture medium containing about 5.0 × 10⁴ cells was seeded on each sample and then subjected to sterilization with 75% ethanol and equilibration in a phosphate-buffered saline (PBS). After the cells attached onto the surface of the sample, the culture medium was replaced by 4 mL of the fresh medium in a six-well culture tissue plate. After 1 day and 3 days of culturing time, the samples were rinsed with PBS, fixed with 2% paraformaldehyde, and immunofluorescently stained for the cytoskeleton protein f-actin with phalloidin-fluorescein isothiocyanate (Sigma). The nuclei were counterstained with hoechst33342. The cell morphology was determined using a digital camera (Carl Zeiss Axioplan 2).

**RESULTS AND DISCUSSION**

**Structure of the coating**

The Raman spectrum (200–800 cm⁻¹) acquired from the coated sample is shown in Figure 1. The band centered at about 475 cm⁻¹ indicates that the coating is mainly amorphous silicon. The FTIR spectrum from 400–2600 cm⁻¹ is displayed in Figure 2. The absorption band at 650 cm⁻¹ originates from the wagging modes of silicon hydrides (isolated monohydride, Si—H; dihydride, Si—H₂, and clustered monohydrides, (Si(H)ₓ). The band at 890 cm⁻¹ arises from the bending mode of silicon dihydride. The broad absorption band from 1900 to 2300 cm⁻¹ is mainly attributed to the stretching mode of silicon hydrides including isolated monohydride (2000 cm⁻¹) and dihydride (2100 cm⁻¹) and/or clustered monohydrides (2090 cm⁻¹).24 Because of residual oxygen in the deposition chamber, silicon oxide bands also appear in the spectrum. The bands at 1004 and 1200 cm⁻¹ arise from Si—O—Si and Si=O respectively.25 The presence of Si—H bonds provides a bioactive surface on the coating.19 When soaked in SBF solution, the =Si—H structure is first hydrated to form silanol (=Si—OH) via the following reaction:

$$\text{Si} - \text{H} + \text{H}_2\text{O} \rightarrow \text{Si} - \text{OH} + \text{H}_2$$

Afterwards, the silanol reacts with the hydroxylion to produce a negatively charged hydrated surface with the functional group —Si—O⁻:19

$$\text{Si} - \text{OH} + \text{OH}^- \rightarrow \text{Si} - \text{O}^- + \text{H}_2\text{O}$$

Subsequently, calcium ions in the surrounding SBF are attracted to the negatively charged surface sites, followed by the arrival of HPO₄²⁻, resulting in the formation of a hydrated precursor cluster con-

![Figure 1. Raman spectrum of the hydrogenated amorphous silicon-coated AZ91 magnesium alloy](image1)

**Figure 1.** Raman spectrum of the hydrogenated amorphous silicon-coated AZ91 magnesium alloy.

![Figure 2. FTIR spectrum acquired from the hydrogenated amorphous silicon-coated AZ91 magnesium alloy](image2)

**Figure 2.** FTIR spectrum acquired from the hydrogenated amorphous silicon-coated AZ91 magnesium alloy.
sisting of calcium hydrogen phosphate. After the precursor clusters are formed, they spontaneously grow by consuming calcium and phosphate ions from the body fluids in the vicinity.\textsuperscript{19}

Figure 3 depict SEM micrographs of the as-deposited coating. No pores can be seen from both the low and high magnification views. The as-deposited coating is dense, smooth, and uniform. The cross-sectional views in Figure 4 reveal that the film is about 1-\mu m thick. Again, no pores and cracks can be seen from the cross-sectional views. The EDS line scans across the interface discloses that the magnesium content diminishes gradually and the silicon content goes up gradually from the Mg substrate side to the Si coating side. Some silicon and magnesium interdiffusion thus takes place during deposition. In the magnesium-silicon phase diagram, three phases of the intermetallic compound, namely Mg\textsubscript{2}Si, Mg, and Si exist, and both Mg and Si have almost negligible solid solubility in each other.\textsuperscript{26}

Hence, interdiffused magnesium and silicon cannot exist as isolated atoms but rather as Mg\textsubscript{2}Si. The

\textbf{Figure 3.} SEM micrographs of the hydrogenated silicon-coated AZ91 magnesium alloy: (a) low magnification; (b) high magnification.

\textbf{Figure 4.} Cross-sectional SEM micrographs of the hydrogenated silicon-coated AZ91 magnesium alloy: (a) low magnification; (b) high magnification.
formation of Mg$_2$Si strengthens the chemical bond between the substrate and coating enhancing adhesion of the coating.

Vickers hardness and water contact angle measurement

The Vickers hardness values determined from the AZ91 magnesium alloy and hydrogenated amorphous silicon coated AZ91 magnesium alloy are shown in Table II. The AZ91 magnesium alloy substrate has very low hardness of only 57 HV. The hardness of the coating is much higher than that of the substrate reaching about 540 HV. Hence, the coated alloy is mechanically much stronger. It is desirable for biomaterials to have a hydrophilic surface as a hydrophilic surface may enhance cell adhesion by optimizing initial protein interactions. $^{27}$ Hence, the water contact angle is measured at room temperature. The mean water contact angle of $32 \pm 2^\circ$ is calculated from four measurements, clearly showing that the coated sample is much more hydrophilic. Figure 5 shows a representative water contact angle measurement of the coated sample.

Electrochemical behavior

Representative polarization curves of both the as-cast and as-coated AZ91 magnesium alloy are depicted in Figure 6. The untreated magnesium alloy has a negative corrosion potential in SBF of about $-1836$ mV. The corrosion potential ($E_{corr}$) of the coated sample is much more positive, shifting to about $-1507$ mV. The corrosion current density ($I_{corr}$) of the coated sample ($3.75 \times 10^{-6}$ A cm$^{-2}$) is about two orders of magnitude lower than that of the untreated sample ($7.05 \times 10^{-4}$ A cm$^{-2}$), indicating much lower corrosion rates for the coated sample in SBF compared to the untreated sample.

The corrosion potential ($E_{corr}$) reflects the combined outcome of all the electrochemical reactions taking place at the electrode/solution interface. The variation in the corrosion potential with immersion time can be employed to study what goes on at the electrode/solution interface. The typical $E_{corr} - t$ curves determined from the as-cast and as-coated AZ91 magnesium alloy are shown in Figure 7. It can be seen that the $E_{corr}$ of the as-coated sample is much more positive than that of as-cast sample, which is in good agreement with the results obtained from the potentiodynamic test. At the beginning of immersion, the potential of the uncoated sample increases quickly and then moves to a nobler direction gradually and smoothly as time elapses. At the end of immersion, the potential tends to become constant. When the magnesium alloy is exposed to

![Figure 5](image_url)  
*Figure 5. Representative views of water contact angle measurements. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]*

![Figure 6](image_url)  
*Figure 6. Potentiodynamic polarization curves of the as-coated and uncoated AZ91 magnesium alloy in SBF.*

![Figure 7](image_url)  
*Figure 7. Representative open circuit potential evolution of the as-coated and uncoated AZ91 magnesium alloy as a function of immersion time in SBF.*
the corrosion medium, chemical dissolution together with electrolyte penetration results in spontaneous corrosion on the entire surface quickly.\textsuperscript{23} One byproduct of magnesium dissolution is OH\textsuperscript{−}, which leads to precipitation of the corrosion products as magnesium hydroxide, magnesium phosphate, and magnesium carbonates.\textsuperscript{28} As a result, the active region decreases and protection rendered by the corrosion products layer is enhanced progressively with longer exposure time. This is the reason why the corrosion potential increases gradually with immersion time. After immersion for a sufficiently long time, an equilibrium between substrate dissolution and corrosion products formation is established and then the potential remains constant. The smooth potential curve suggests a general corrosion process during immersion that is not very sensitive to localized corrosion.\textsuperscript{29} Rapidly increasing corrosion potentials can be observed from the as-coated sample during the early stage. This potential–time relationship is probably related to the soaking process on the electrode surface and/or electrostatic effects that give rise to charges at the interface of the dual layer.\textsuperscript{23} Large fluctuations cannot be observed during the entire immersion. The fluctuations reveal that it is difficult for the electrode to establish an equilibrium at the electrode/solution interface that can be attributed to changing of the surface states and exposure environment.\textsuperscript{23} Thus, the stable potential implies a stable state of the coated alloy in the SBF solution arising from the good protection from the deposited coating.

EIS is a powerful technique to study corrosion of metals or coated alloys. It can provide quantitative evaluation of the corrosion properties of the studied system, which may be difficult to assess using conventional electrochemical measurements such as potentiostatic or potentiodynamic techniques. By appropriate interpretation of the EIS data in conjunction with an EC, the detailed information on the corrosion process at the electrolyte/electrode interface can be provided. Furthermore, the EIS test does not appear to significantly accelerate the corrosion reaction and can also be conducted in situ nondestructively. This technique is more effective for the study of localized corrosion via small pores.\textsuperscript{23,30} The representative EIS curves obtained from the as-coated sample as a function of immersion time in SBF are shown in Figure 8. Right from the beginning of immersion, the studied system has three time constants, a capacitive loop at high frequencies, a capacitive loop at medium frequencies, and a pseudoinductive loop at low frequencies. The high frequency behavior of EIS is associated with electrolyte penetration including water uptake and salt intrusion. The properties of the deposited coating and their changes can be determined at high frequencies. The capacitive arcs generally result from charge transfer, film effects, as well as mass transfer. Usually, the low frequency region in the EIS conveys important information on the electrode-controlled process together with the contribution from localized defects to the overall impedance.\textsuperscript{23} The presence of the pseudoinductive loop can probably be ascribed to the existence of relaxation processes involving the absorbed species at the vulnerable region,\textsuperscript{30} indicating nucleation of corrosion pits.\textsuperscript{31}

Considering the physical structure of the electrode system and impedance responses, the EC for fitting the EIS spectra of the as-coated Mg alloy is proposed and illustrated in Figure 9. $C_c$ is one of the constant

Figure 8. Representative EIS spectra of the as-coated AZ91 magnesium alloy as a function of immersion time in SBF.

Figure 9. EC used in the analysis of the EIS spectra of the as-coated AZ91 magnesium alloy.
phase angle CPE components and denotes the capacitance of the intact deposited coating. $R_{po}$ is the relevant resistance or ionic conducting defect resistance. $C_{dl}$ is another CPE component and represents the capacitance of the double layer in the vulnerable regions exposed to the bottom of electrolyte penetration paths. The Faraday charge transfer resistance, $R_t$, which is related to the electrochemical reaction in the same region, is in parallel with $C_{dl}$. $R_s$ is the solution resistance between the reference and working electrode. Its value is decided by the conductivity of the test medium and the geometry of the cell.23 The EIS fitted results of the as-coated AZ91 magnesium alloy are presented in Table III. According to the formula of film capacitance: $C = \varepsilon_0 \varepsilon_r S/d$, where $S$ is the area of the film, $d$ is the thickness, and $\varepsilon_0$ and $\varepsilon_r$ are the dielectric constants in vacuum and of the film, the typical film capacitance is on the order of $1 \mu F \ cm^{-2}$ but varies with $\varepsilon_r$, $S$, and $d$.23 Obviously, the fitted $C_c$ results are in this range. With prolonged exposure time, $C_c$ increases to some extent. This variation of $C_c$ is linked to the enhancement of the dielectric constant of the deposited coating resulting from the penetration of the electrolyte or defect enlarging. The $C_{dl}$ is mainly in the range of typical metal/solution system, from $10 \mu F$ to $100 \mu F$, and increases progressively with longer immersion time. In the beginning, the system shows a high $R_{po}$ indicating good corrosion resistance of the coating. $R_{po}$ decreases only slightly after 18 h of immersion indicating a good state of the whole coating. $R_t$ is related to the electrochemical reactions at the bottom electrolyte penetration paths. The higher the charge transfer resistance, the lower is the corrosion rate. The system also shows high $R_t$ and for long immersion time, $R_t$ decreases dramatically. It is known that PVD coatings often possess growth defects manifested as pores and pinholes through which corrosion attack on the substrate materials takes place. This case is even more severe if the coated system is exposed to an aggressive environment, for instance Cl$^-$ containing corrosion media, because of strong effect of Cl$^-$ in promoting localized corrosion. Because of the much lower corrosion resistance of the magnesium substrate, once corrosion begins at vulnerable sites, even in a tiny area, serious corrosion of the Mg substrate ensues quickly leading to the exfoliation of the coating in the vicinity and the damaged site develops quickly leading to a fast drop in $R_t$. Combining the variation of $R_{po}$ and $R_t$, it can be inferred that the deterioration mechanism of the deposited coating is mainly in the form of vulnerable sites developing or enlarging. Here, $m$ and $n$ are indices of the dispersion effect of the CPE components, $C_c$ and $C_{dl}$, respectively representing their deviations from the ideal capacitance because of the inhomogeneity and roughness of the electrode on the microscale. The values of $m$ and $n$ are always $0 < m, n < 1$. It is evident that the values of $m$ and $n$ in our experiments are in this range.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>$R_s$ ($\Omega \ cm^2$)</th>
<th>$C_c$ (10$^{-6}$ F cm$^{-2}$)</th>
<th>$m$</th>
<th>$R_{po}$ (k$\Omega$ cm$^2$)</th>
<th>$C_{dl}$ (10$^{-6}$ F cm$^{-2}$)</th>
<th>$n$</th>
<th>$R_t$ (k$\Omega$ cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>152.1</td>
<td>2.401</td>
<td>0.7482</td>
<td>8.712</td>
<td>41.35</td>
<td>0.9079</td>
<td>6.432</td>
</tr>
<tr>
<td>6</td>
<td>177.3</td>
<td>3.104</td>
<td>0.7684</td>
<td>10.05</td>
<td>81.37</td>
<td>0.9093</td>
<td>5.696</td>
</tr>
<tr>
<td>12</td>
<td>174.0</td>
<td>3.693</td>
<td>0.8062</td>
<td>7.750</td>
<td>150.4</td>
<td>0.9241</td>
<td>1.323</td>
</tr>
<tr>
<td>18</td>
<td>170.8</td>
<td>5.366</td>
<td>0.7615</td>
<td>7.452</td>
<td>178.9</td>
<td>0.9430</td>
<td>2.193</td>
</tr>
</tbody>
</table>

Table III

EIS Fitted Values of the As-Coated AZ91 Magnesium Alloy

![Figure 10. Representative EIS spectra of the uncoated AZ91 magnesium alloy as a function of immersion time in SBF.](image)
For comparison, EIS spectra of the as-cast sample are shown in Figure 10. Similar to the impedance spectrum of the as-coated alloy, there are three time constants, a capacitive arc in the high frequency region, a capacitive arc in the middle frequency region, and a pseudoinductive arc in the low frequency region. It is noted that both the two capacitive arcs increase with longer exposure durations. However, the inductive loop gradually diminishes with longer immersion time. After immersion in SBF, corrosion takes place on the entire surface of the sample. The by-product of magnesium dissolution, OH\(^{-}\), induces precipitation of magnesium hydroxide, magnesium phosphate, and magnesium carbonates.\(^{30}\) The capacitive arcs are attributed to charge transfer, film effects, as well as mass transfer in the corrosion products layer, respectively. The presence of the inductive loop arises from dissolution and formation of the corrosion product layer at vulnerable regions. The corrosion product layer can inhibit dissolution of the substrate to some extent and with longer immersion time, the corrosion product layer thickens gradually and it is the reason of the two capacitive arcs increasing with exposure time. In addition, with increasing immersion time, the vulnerable regions decrease and the dissolution and precipitation process also diminish gradually leading to reduction in the inductive loop.

Cytocompatibility behavior

The high degradation rates of magnesium alloys in a physiological environment are the main limitations for their applications to biodegradable hard tissue implants. In contact with the culture media, severe corrosion frequently takes place on the untreated alloy followed by the evolution of hydrogen gas. As aforementioned, the by-products of mag-

Figure 11. Cell morphology on AZ91 magnesium alloy after 1 day of culture. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 12. Cell morphologies after 1 day and 3 days of culture on as-coated AZ91 magnesium: (a) 1 day, low magnification; (b) 1 day, high magnification; (c) 3 days, low magnification; (d) 3 days, high magnification. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
nesium dissolution, OH\textsuperscript{−}, enhances the pH value of the culture media significantly. It is known that cells are very sensitive to such environmental fluctuations.\textsuperscript{32} This significant enhancement in the pH value leads to fatal effects on the viability of cell. During magnesium dissolution, the media contain a very high concentration of magnesium ions. In addition, corrosion of magnesium leads to the formation of a corrosion products layer.\textsuperscript{30} The formed corrosion product gradually falls out from the surface due to the severe mismatch between the substrate and corrosion product layer.\textsuperscript{30} The formed corrosion product and departure process make it difficult for cells to attach on the surface. The high hydrogen evolution rate also affects cell attachment and proliferation. All these reasons account for the observation that no cells survive after seeding on the untreated alloy for 1 day, as demonstrated in Figure 11. Obviously, serious corrosion also appears on the uncoated sample. The cell morphology on the coated AZ91 magnesium alloy after 1 day and 3 days of culture is displayed in Figure 12. The cells are observed to attach well on the coating and proliferate normally as a result of the improved corrosion resistance of the coated sample as described previously and consequently better biocompatibility. Our results indicate favorable biocompatibility and desirable protection effects of the coated sample.

CONCLUSION

Biocompatible, corrosion-resistant hydrogenated amorphous silicon coatings about 1-μm thick have been successfully deposited on AZ91 magnesium alloy. The structure of the coating, electrochemical behavior in SBF, and cytocompatibility are studied. The surface hardness of the coated alloy is enhanced significantly and the coated surface is quite hydrophilic as well. The corrosion resistance of the coated alloy is dramatically improved. The EIS results reveal that deterioration of the coating is mainly in the form of localized defect development or enlargement. Favorable cytocompatibility and normal cell proliferation are observed on the coated alloy as demonstrated by cell culture tests.

References