Rapid In Vitro Corrosion Induced by Crack-Like Pathway in Biodegradable Mg–10% Ca Alloy

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Abstract: The in vitro corrosion mechanism of the biodegradable cast Mg–10% Ca binary alloy in Hanks’ solution was evaluated through transmission electron microscopy observations. The corrosion behavior depends strongly on the microstructural peculiarity of Mg2Ca phase surrounding the island-like primary Mg phase and the fast corrosion induced by the interdiffusion of O and Ca via the Mg2Ca phase of lamellar structure. At the corrosion front, we found that a nanosized crack-like pathway was formed along the interface between the Mg2Ca phase and the primary Mg phase. Through the crack-like pathway, O and Ca are atomically exchanged each other and then the corroded Mg2Ca phase was transformed to Mg oxides. The in vitro corrosion by the exchange of Ca and O at the nanosized pathway led to the rapid bulk corrosion in the Mg–Ca alloys.

Key words: magnesium alloy, corrosion mechanism, in vitro, TEM, EELS, interdiffusion, crack-like pathway

INTRODUCTION

Recently, biodegradable materials such as Mg and its alloys have emerged for various implantable applications in orthopedic fixatives and cardiovascular devices (Witte et al., 2005; Staiger et al., 2006). However, there is a lack of knowledge regarding nanoscale corrosion and biological evaluation method (Nie & Muddle, 1997; Kim et al., 2008; Li et al., 2008; Gu et al., 2009, 2010). As biodegradable materials dissolve over the implantation period in the living body, various characterizations are required for biological safety evaluation of medical devices, based on a recently revised ISO 10993-1 guideline.

In general, a unique biodegradability of Mg alloy is originated from the corrosion property that Mg atoms are dissolved by the oxidation as a following chemical reaction equation (Staiger et al., 2006):

\[ \text{Mg} + 2\text{H}_2\text{O} = \text{Mg(OH)}_2 + \text{H}_2 \]

The evolution of hydrogen gas in the equation can cause a problem when biodegradable metal alloys are used as an implantable device for human body with high corrosion rate because it can induce abnormal gas pockets in the subcutaneous tissue (Witte et al., 2005).

Although it is very important to understand the reaction that affects the biodegradable properties, the detailed corrosion reaction in the Mg–Ca alloy is not revealed yet. Furthermore, as H2O molecules cannot diffuse into the metal’s internal area, this corrosion reaction reported by many researchers can be valid only at the Mg surface (Witte et al., 2005; Kannan & Raman, 2008; Kim et al., 2008). On the corrosion mechanism of the Mg–Ca alloy, we simultaneously performed in vivo study showing that the alloy is rapidly corroded by the interdiffusion of O and Ca via the Mg2Ca phase in femoral condyle of the rabbit. However, it did not show direct evidences of how to transport O to the corrosion front.

On the other hand, most studies on biodegradable implant materials have mainly concentrated on using the techniques such as computer tomography and magnetic resonance imaging in order to characterize reaction products at corrosion surface (Witte et al., 2006). These techniques allow a macroscopic corrosion observation in the living body, but do not provide any information regarding degradation and reaction products in the atomic scale. Thus, in this study, the in vitro corrosion mechanism of the Mg–Ca alloy is thoroughly investigated by using electron microscopy (EM), which allows observation from atomic scale to macroscopic scale simultaneously.

MATERIALS AND METHODS

Mg and Ca wt% ratio of 90 to 10 were mixed, melted, and cast in vacuum melting furnace in argon atmosphere. For in vitro corrosion test, the cast ingot was submerged into...
Hanks’ solution, which is utilized for simulating body fluid conditions, for 3 h. Then, the pretreated samples for EM observation were investigated by using electron probe microanalyzer (EPMA, JXA-8500F, JEOL, Japan) and back-scattered electron detector equipped in focused ion beam (FIB, Quanta 3D, FEI Company, USA) system, including scanning electron microscopy (SEM). For more chemical detail, elemental maps were acquired by energy-dispersive spectroscopy (EDS, equipped in FIB). Transmission electron microscopy (TEM; Titan, FEI Company, USA) observations were performed from special samples prepared by FIB at the front area of corrosion. In particular, electron energy-loss spectroscopy (EELS, GIF866, Gatan, USA) technique was used to confirm the elemental distribution in atomic scale.

Lastly, all crystalline phases of corrosion products were identified with selected area diffraction (SAD) analysis.

RESULTS AND DISCUSSION

As mentioned in our previous results, the cast microstructure of Mg–Ca 10% alloy in EPMA compositional image of Figure 1a mainly consists of a primary Mg phase and a eutectic phase, which includes a lamellar Mg (L-Mg) and a lamellar Mg$_2$Ca (L-Mg$_2$Ca) phase. Figure 1b is a cross-sectional scanning electron microscopy image of the Mg–Ca alloy corroded for 3 h in Hanks’ solution. The corrosion direction is marked by two black-dotted arrows and the corrosion front is also marked by white-dotted line. The magnified image in the inset of (b) shows all phases existing on the Mg–Ca alloy.

Figure 1. a: An electron probe microanalyzer compositional image of the cast Mg–10 wt% Ca alloy, which shows primary Mg phase (α–Mg) of dark gray color and a eutectic phase of white color, including a lamellar Mg (L-Mg) and a lamellar Mg$_2$Ca (L-Mg$_2$Ca) phase. b: A cross-sectional scanning electron microscopy image of the Mg–Ca alloy corroded for 3 h in Hanks’ solution. The corrosion direction is marked by two black-dotted arrows and the corrosion front is also marked by white-dotted line. The magnified image in the inset of (b) shows all phases existing on the Mg–Ca alloy.

Figure 2. (a) A scanning electron microscopy image and (b–d) energy-dispersive spectroscopy elemental maps of Mg, Ca, and O at the corrosion front. c, d: Four transmission electron microscopy samples were prepared at regions with different corrosion rate. Two white-dotted arrows (in (a)) indicate the corrosion direction from interface to internal area of the alloy.
lamellar Mg phase. On the contrary, the lamellar Mg has a very similar gray color compared with the primary Mg phase as shown in the enlarged inset of Figure 1b. It means that there is no any corrosion phenomenon in the lamellar Mg phase yet. Interestingly, another Mg2Ca phase, named as wrapping Mg2Ca phase indicated by a series of four white-dotted arrows in Figure 1b, exists at the surface surrounding the primary Mg phase. This phase is distinguished from the lamellar Mg2Ca, having the same crystal structure.

As seen in Figure 2, the elemental distribution at the corrosion front was investigated using EDS maps. There are two white-dotted arrows to indicate corrosion direction. Extensive observation of microscopic elemental movement after corrosion indicated that O came into the alloy and most of the internally existing Ca is depleted. That is, the wrapping Mg2Ca surrounding the primary Mg phase and the lamellar Mg2Ca are corroded by interdiffusion of Ca and O. In addition, Mg and O elemental maps in Figure 2b and 2d clearly show the corrosion frontline as shown in Figure 1b. The corrosion rate of the wrapping Mg2Ca is relatively faster than the normal lamellar Mg2Ca, although both have the same crystal structure and chemical composition. The corrosion behavior observed in Figure 2 reveals that in vitro corrosion of the alloy submerged in Hanks’ solution seems to be very close with in vivo corrosion (Jung et al., 2012). For detailed examination, we distinguished four regions having different corrosion states and then labeled them from region 1 to region 4. Those labels will be used in TEM observations and EELS elemental maps in Figure 3. The chemical distribution and corrosion state at each region is summarized in Table 1.

From EDS maps of Figure 2, region 1 does not seem to be macroscopically corroded, and both regions 2 and 3 are corroded by O penetration into the wrapping Mg2Ca phase. In those regions, the opposite distribution of O and Ca is very similar to our findings in the previous study, which proposed the interdiffusion mechanism of O and Ca via Mg2Ca phase. However, coexistence of O and Ca in region 2 does not seem to match with our previous findings as it means that Ca can still remain in the area after corrosion. It is attributed to the limitation of SEM observation due to the reaction volume of electron and sample. As shown in Figure 3, therefore, we adopted TEM and EELS observations to discuss in more detail. Lastly, region 4 is considered a perfectly corroded area originating from the wrapping Mg2Ca.
To begin with, we found that the TEM images in Figure 3 show various corrosion states of the Mg–Ca alloy submerged in Hanks’ solution for only 3 h. It is a critical point to understand the change of Mg2Ca phase for the knowledge of corrosion behavior in Figures 3a–3d. In Figures 3a, 3e, and 3i, TEM allows us to observe a nanosized crack-like pathway, which is developing at the wrapping Mg2Ca. This nanosized pathway may be the first signal of in vitro corrosion, which nobody finds. In our findings, the pathway propagates along the interface between the wrapping Mg2Ca and the primary Mg, which may contain internal stress by lattice mismatch between two phases or irregular distribution of chemical composition. By the characterization of SAD pattern in Figure 3i showing the pathway tip, the wrapping Mg2Ca phase with a single crystalline structure is transformed to polycrystalline MgO phase. It reveals that the pathway acts as a “highway” for O diffusion. Schematic descriptions in Figures 3m–3p will provide the geographical information of each phase of the specimens for further understanding.

The corrosion pathway shown in Figure 3b became thicker than Figure 3a and clearly contained the higher O concentration, meaning more corroded state. The remaining half layer of the wrapping Mg2Ca keeps the original Mg2Ca state without the change of crystal structure and chemical composition. On the other hand, especially in the corroded layer, Ca in Mg2Ca and O in Hanks’ solution are exchanged by the interdiffusion along the crack-like pathway. As a result, nanocrystalline Mg oxide was formed, as shown in a SAD pattern of Figure 3j. In addition, there are a few small holes and CaO phase.

In Figure 3c, showing the region 3, Ca is rarely found on the whole sample and O is perfectly packed into the Mg2Ca phase. There are bigger holes and more amount of CaO phase when compared with Figure 3b. The most corroded area in Figure 3g is transformed to Mg oxide. Its enlarged image and SAD pattern in Figure 3k shows the same results as reported earlier (Witte et al., 2005; Staiger et al., 2006; Li et al., 2008; Gu et al., 2009). Lastly, Figure 3d, which represents the completely corroded area, no longer contained Ca in the Mg2Ca phase and most area became nanocrystalline MgO as shown in Figure 3l. Figures 3a–3d and 3m–3p obviously show a sequential progress of O diffusion into the wrapping Mg2Ca and the lamellar Mg2Ca through the crack-like pathway. In the final stage of corrosion, the lamellar Mg was also corroded and then transformed to Mg oxide. This was confirmed from a homogeneous contrast of Mg oxide observed in the lamellar area of Figure 3d.

The corrosion rate of the wrapping Mg2Ca phase was always faster than that of the lamellar Mg2Ca phase. We strongly assume that it is due to the internal stress or the chemically different composition between different phases such as the primary Mg and the wrapping Mg2Ca. Such conditions at interface may slightly induce the potential difference and can easily make the crack-like pathway (Jung et al., 2012). The Mg2Ca phase in Mg–Ca alloy is selectively corroded by making the pathway, by generating rapid interdiffusion of Ca and O into the alloy, and then by expanding the corrosion toward the inside of the lamellar Mg2Ca.

**CONCLUSION**

Biodegradable Mg–10 wt% Ca binary alloy was cast and was immersed in Hanks’ solution for the evaluation of in vitro corrosion. The alloy consisted of a primary Mg phase and eutectic lamellar structure. The lamellar Mg2Ca phase corroded faster than the primary Mg phase and the lamellar Mg phase by the interdiffusion of Ca and O. The in vitro corrosion mechanism was very similar to in vivo corrosion mechanism. In particular, we found a crack-like pathway, leading to the interdiffusion of O and Ca, in the wrapping Mg2Ca phase surrounding the primary Mg phase. Finally, we can expect that all phases existing in the alloy will be transformed into polycrystalline Mg oxide after in vitro corrosion.

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REFERENCES


