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Biodegradation of Secondary Phase Particles in Magnesium Alloys: A Critical Review

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Magnesium alloys have been extensively studied in recent years for potential biodegradable implant applications. A great deal of work has been done on the evaluation of the corrosion behaviour of magnesium alloys under in vitro and in vivo conditions. However, magnesium alloys, in general, contain secondary phase particles distributed in the matrix and/or along the grain boundaries. Owing to their difference in chemistry in comparison with magnesium matrix, these particles may exhibit different corrosion behaviour. It is essential to understand the corrosion behaviour of secondary phase particles in magnesium alloys in physiological conditions for implant applications. This paper critically reviews the biodegradation behaviour of secondary phase particles in magnesium alloys.

Keywords : *magnesium alloys, biomaterial, corrosion, secondary phase particles, galvanic corrosion*

1. Introduction

Metallic magnesium has similar mechanical properties to natural bone than that of the traditional metallic biomaterials such as stainless steels and titanium alloys1). Importantly, magnesium corrodes in body fluid and the corrosion product is non-toxic. Further, magnesium is an essential element for the human body and it has been shown to improve bone strength1,2). These attractive properties of magnesium make it a potential candidate for biodegradable implant applications. However, the main issue with pure magnesium is that it corrodes rapidly in physiological conditions, which makes it to fail before the expected service period. In addition, due to the high corrosion rate of magnesium, the cathodic reaction of magnesium, i.e., hydrogen evolution, creates gas pockets near the magnesium-based implants, which can affect the bone healing process2). Hence, it is necessary to decrease the degradation rate of magnesium for making it suitable for implant applications.

Over the past decade, a number of magnesium alloys have been tested under in vitro and in vivo conditions to understand their corrosion behaviour. Among the magnesium alloys studied, AZ (aluminium, zinc) series magnesium alloys are the most highly researched material due to their commercial availability3-5). A wide range of rare-earth containing magnesium alloys, e.g. ZE41, WE43, WE54 and LAE442 (containing rare-earth mixtures such as cerium, lanthanum, ytterbium, neodymium and praseodymium) have also been studied6-8). In recent years, magnesium-calcium alloys have gained high interest due to their excellent biocompatibility9,10). Calcium, which is a major component in natural bone, not only makes the alloys highly biocompatible, but has also shown to improve the corrosion resistance of the alloys9).

2. Secondary phase particles

Most of the magnesium alloys that have been studied for biodegradable implant applications contain secondary phase particles : for example, $Mg_{17}Al_{12}$ (β-phase) in AZ series alloy11,12), $Mg_{12}YNd$ and $Mg_{14}YNd_2$ in WE43 alloy13), and Mg_2Ca in Mg-Ca alloys14). The in vitro and in vivo degradation studies carried out on these secondary phase particles containing magnesium alloys have only focused on the overall corrosion behaviour of the alloy. Since these secondary phase particles have different chemical composition as compared to magnesium matrix, these particles may have different corrosion rates.

Literature suggests that secondary phase particles in magnesium alloys are cathodic to the matrix and hence are more corrosion resistant than the alloy matrix15,16). For example, in chloride-containing solution the β-phase (com-

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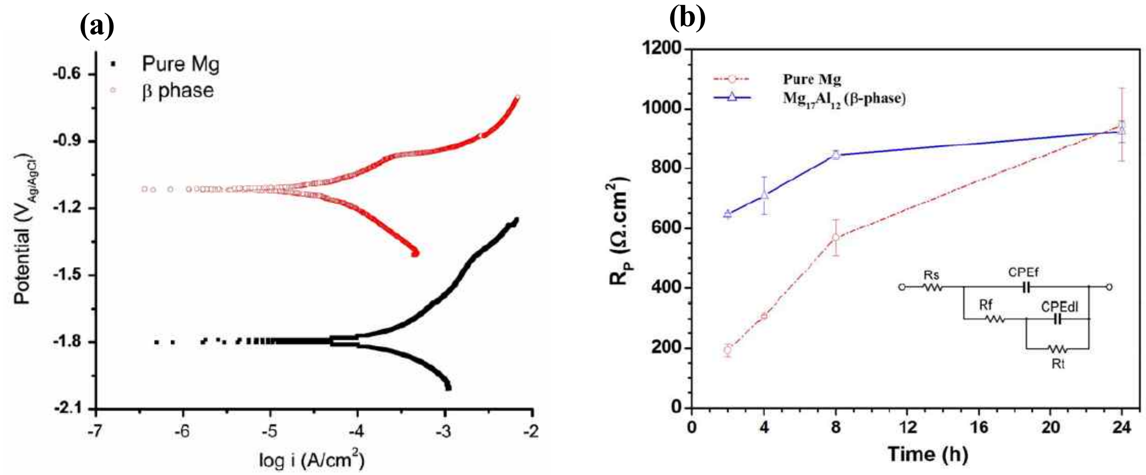

Fig. 1. Electrochemical degradation behaviour of β-phase and pure magnesium in SBF: (a) potentiodynamic polarisation curves[23], and (b) polarisation resistance from EIS results[24].

monly present in AZ series magnesium alloy) exhibited an electrochemical potential which is 490 mV noble to pure magnesium[17]. It has also been reported that the volume fraction of secondary phase particles in magnesium alloys plays a crucial role in the alloy corrosion resistance. A large volume fraction of secondary phase particles improves the corrosion resistance of the alloy by acting as a stable barrier, i.e., corrosion of the magnesium matrix would lead to complete coverage of stable secondary phase particles on the alloy. On other hand, the corrosion rate of the alloy increases continuously if the volume fraction of secondary phase particles is low. In this case, the secondary phase particles would act as a cathodic site and increase the corrosion[18].

Another phenomenon has been observed in zirconium-containing magnesium alloys[19]. A lower corrosion attack was seen in microstructure containing a homogeneous distribution of small zirconium particles, whereas the corrosion attack was high when zirconium is concentrated. It has also been reported that in zirconium containing magnesium alloys, zirconium-rich regions in the microstructure exhibited higher corrosion resistance than the zirconium depleted regions[20]. Coy et al[21] found that zirconium-rich precipitates exhibit a volta potential of 170 mV noble to that of the magnesium matrix, which they attributed to the presence of impurities such as iron, nickel and silicon in the zirconium-phase intermetallics.

3. In vitro corrosion

Recently, Kannan[11] examined the effect of microstructure on the *in vitro* corrosion behaviour of AZ91 magnesium alloy. It was found that β-phase particles were stable as compared to the magnesium matrix in simulated body fluid (SBF), which is similar to that reported in chloride-containing solution[18]. The magnesium alloy (AZ91) containing a large volume fraction of β-phase exhibited a stable network of the secondary phase particles after polarisation test. In order to understand the corrosion behaviour of β-phase alone, Kannan et al[23] prepared β-phase intermetallic and examined the in vitro corrosion behaviour. They found that the β-phase was noble by 680 mV to pure magnesium. Comparing with the potential difference observed for this system in sodium chloride solution[17], the difference in SBF is higher (~ 190 mV). Interestingly, potentiodynamic polarisation results showed that both pure magnesium and β-phase exhibited breakdown potentials in the anodic region. However, β-phase exhibited lower anodic current of as compared to that of pure magnesium. Hence, β-phase exhibited ~ 80 % lower corrosion rate than that of pure magnesium.

Electrochemical impedance spectroscopy (EIS) results also confirmed the higher corrosion resistance of β-phase than pure magnesium, i.e., a threefold increase in the polarization resistance was observed[23]. In order to understand the long-term corrosion behaviour of β-phase, Walter and Kannan[24] carried out EIS experiments and found that the polarisation resistance for both β-phase and pure magnesium increased with increase in exposure time. But, the difference in the polarisation resistance decreased with increase in exposure time. After 24 h exposure, the polarisation resistance of β-phase was similar to that of pure magnesium.

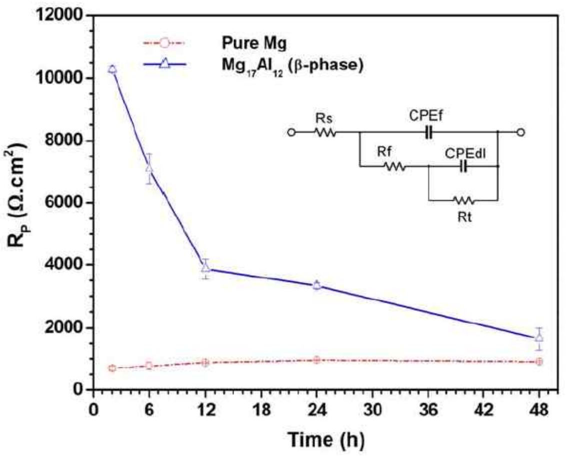

Fig. 2. Polarisation resistance of β-phase and pure magnesium after galvanically coupled in SBF for 24 h[24].

4. Galvanic corrosion

Micro-galvanic corrosion can be expected in magnesium alloys in physiological conditions since there is a significant difference in the electrochemical potential between secondary phase particles and matrix in magnesium alloys. Walter and Kannan[24] investigated the micro-galvanic corrosion of β-phase and pure magnesium system. They galvanically coupled β-phase and pure magnesium in SBF. Pure magnesium corroded significantly over the exposure period, while a white powder layer was formed on the β-phase. Chemical analysis confirmed that the powder is mainly composed of phosphate and carbonate. The authors have also studied the corrosion behaviour of β -phase and pure magnesium after decoupling the samples. It was observed that the polarisation resistance for pure magnesium was relatively constant during the 48 h testing period, whereas for β-phase the initial polarisation resistance was significantly higher, which was attributed to the formation of the phosphate/carbonate layer. But, this high resistance rapidly dropped over time and was similar to that of the pure magnesium by 48 h immersion. Based on these results, the authors suggested that that the phosphate/carbonate layer formed on β-phase during galvanic coupling is poorly protective. Kalb et al[13] studied the mi-

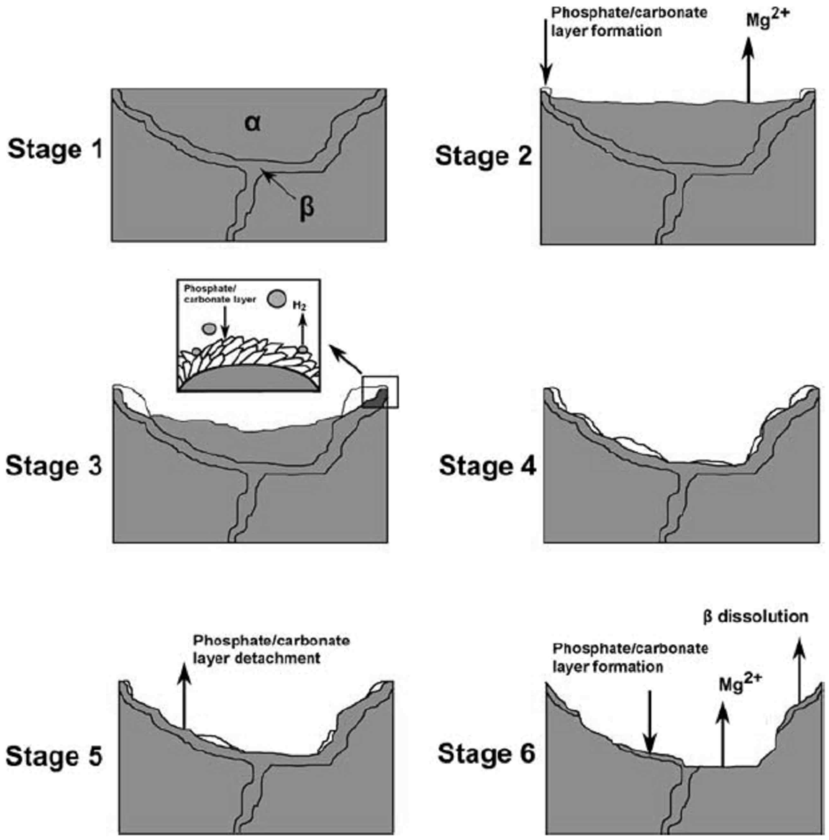

Fig. 3. A phenomenological model explaining the mico-galvanic corrosion in AZ series magnesium alloys containing secondary phase particles[24].

cro-galvanic behaviour in a rare-earth containing alloy (WE43). They reported that the cathodic particles (rich in Zr and contain Fe and Ni) in WE43 act as effective micro-galvanic cathodes. The vicinity of the cathodic particles was found to be protected from corrosion, which they attributed to the increase in pH value due to magnesium corrosion.

Walter and Kannan[24)] presented a phenomenological model to explain the micro-galvanic corrosion in magnesium alloys containing cathodic secondary phase particles (Fig. 3). They suggested that the micro-galvanic coupling between the anodic α-phase and the cathodic β-phase increases the corrosion close to the α/β interface. The corrosion of the α-phase produces hydrogen gas on the β-phase, which will lead to a pH rise and then deposition of phosphate/carbonate layer on β-phase occurs. As the α-grains undergo corrosion, the phosphate/carbonate layer will also grow. But, high corrosion of α-grains will reduce the micro-galvanic effect, which leads to the next stage, i.e., detachment of the phosphate/carbonate layer. Once the β -phase is no longer protected by phosphate/carbonate layer or micro-galvanic coupling, corrosion of β-phase occurs eventually and exposes the underlying α-grains, and the corrosion steps described above will be repeated.

5. Summary

Secondary phase particles in magnesium alloys are generally cathodic to that of the magnesium matrix. Hence, during the initial corrosion of the alloy, these particles will enhance the dissolution of α- matrix due to micro-galvanic corrosion. These secondary phase particles will be protected not only cathodically but also by phosphate/carbonate deposition on those particles, but the protection by the phosphate/carbonate layer is only temporary. After high dissolution of α- matrix, these secondary phase particles will eventually dissolve. It is important to know that the secondary phase particles dissolve, because undissolved particles in the body can lead to adverse tissue reactions.

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