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Viewpoint - Understanding Mg corrosion in the body for biodegradable medical implants

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ABSTRACT

Accurate prediction of Mg corrosion rates within the body (*in vivo*) based on laboratory tests (*in vitro*) is a key challenge for Mg alloys in medical applications. Estimates based on *in vitro* measurements overestimate the measured Mg corrosion rate *in vivo*. This indicates that the medical environment and the biocorrosion mechanism is not fully characterised. We summarise (i) the relevant Mg metallurgy, and (ii) the solution factors that influence Mg corrosion *in vitro*. We analyse the reasons for the disparity between the corrosion rates *in vivo* and the expected corrosion rates based on *in vitro* testing, and suggest promising areas of research.

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1. Introduction

This paper addresses the difference between the expectations for the Magnesium (Mg) corrosion rate *in vivo* (based from *in vitro* measurements) and the actual measured Mg corrosion rate *in vivo*.

Understanding the Mg corrosion rate *in vivo* is a critical issue for Mg as a biodegradable metal for medical implants. This application for Mg alloys is an active area of research, development and implementation [1–3]. Overviews of progress are provided by Witte and co-workers [1,2,4]. The concept is that the medical implant corrodes away after it has carried out its function in the body, and is no longer needed. This requires that it is possible to predict the *in vivo* corrosion behaviour of the Mg-implant, based on laboratory testing, *i.e.* based on *in vitro* testing.

Prediction of *in vivo* Mg biocorrosion by a laboratory (*in vitro*) test is possible, if the corrosion mechanism of the Mg in the *in vitro* tests is the same as in the body, *i.e. in vivo*. Thus, it is important to clarify all the factors of importance to the biocorrosion of Mg alloys in the body, *i.e. in vivo*.

The factors pertinent to *in vivo* Mg biocorrosion are summarised herein, based on our present understanding of Mg corrosion [5–17] and informed by recent research [18–37]. The next sections present these factors that include: (i) the metallurgy that governs Mg corrosion, and (ii) the key solution factors that have been identified with respect to Mg biocorrosion *in vitro*. Thereafter, an evaluation is made of the Mg

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https://doi.org/10.1016/j.scriptamat.2018.05.021 1359-6462/© 2018 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved. biocorrosion rates *in vivo*, and a discussion is presented regarding the disparity between *in vitro* and *in vivo* biocorrosion rates.

2. Metallurgical factors

The study of the influence of metallurgical factors on Mg alloy corrosion has typically been carried out in a wide variety of solutions, including concentrated chloride solutions. Although these solutions are different to body fluids, this research nevertheless has elucidated the metallurgical factors which influence Mg biocorrosion [5,6,10–12].

The important metallurgical factors are: (i) the intrinsic reactivity of Mg, (ii) the influence of surface films, (iii) the presence of second phases, particularly including second phases based on the impurity elements (Fe, Ni, Cr and Co), (iv) the influence of alloying elements on protectiveness of the surface films formed on the alloy surface during corrosion, (v) grain size (decreasing grain size can decrease the corrosion rate by a factor of ~four [38–41]), and (vi) texture/crystallography (basal planes have a corrosion rate a factor of ~two lower than less highly packed planes [42–44]).

The intrinsic reactivity of Mg is high, so that Mg has a high tendency to corrode in aqueous solutions [12]. Additionally, the corrosion product films of Mg typically provide little protection against corrosion in aqueous solutions [12].

The intrinsic corrosion rate of Mg is shown in Fig. 1(a) [45] as that of ultra-high purity Mg (0.3 mm/y) and high-purity (HP) Mg (0.4 mm/y) in 3.5% NaCl saturated with Mg(OH)₂. Fig. 1(a) also shows the corrosion rates of sputter deposited MgY and MgGd alloys, and MgY and MgGd



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Fig. 1. (a) The intrinsic corrosion rate of Mg as demonstrated by that of ultra-high purity Mg (the diamond)(0.3 mm/y) and high-purity Mg (0.4 mm/y) in 3.5% NaCl saturated with Mg(OH) 2; compared with the corrosion rates of sputter deposited MgY and MgGd alloys, and MgY and MgGd ingot alloys in the same solution. Corrosion rates were measured from weight loss (full symbols) and hydrogen evolution (open symbols). [45] (b) Corrosion rates [9] of commercial and binary Mg alloys compared with those of High-Purity (HP) Mg and Ultra-High-Purity (UP) Mg in concentrated chloride solutions. There is no Mg alloy with a corrosion rate substantially lower than the intrinsic corrosion rate of Mg in such solutions of 0.3 mm/y. There are some binary and commercial Mg alloys with comparable corrosion rates. Note that, at the low corrosion rates, the corrosion rates measured by hydrogen evolution are typically somewhat too small.

ingot alloys. The sputter deposited alloys had corrosion rates similar to that of HP Mg because all the alloying was in super-saturated solid solution in the alpha-Mg. In contrast the MgY and MgGd ingot alloys had higher corrosion rates, because of the micro-galvanic corrosion due to the second phases [45].

Mg alloys typically have corrosion rates substantially higher than that of high-purity (HP) Mg, as illustrated in Fig. 1(a) and (b) [9]. This is because Mg alloys contain the alpha-Mg matrix, one or more additional phases, and may contain phases associated with the impurity elements (Fe, Ni, Cu and Co) if their concentrations are greater than the (composition-dependent) impurity limits. These additional phases accelerate the corrosion of the alpha-Mg matrix by micro-galvanic corrosion, and typically cause substantial corrosion rates as illustrated in Fig. 1 [9].

High-Purity (HP) Mg contains only alpha-Mg. HP Mg contains no Ferich BCC second phase, no other phase, and no other phase associated with the other impurity elements [5–8,11,12]. HP Mg defines the intrinsic corrosion rate of Mg, and has a corrosion rate of ~0.4 to 0.8 mm/y in 3.5% NaCl saturated with Mg(OH)₂ [5,47,53]. We source HP Mg ([Fe] ~ 20 ppm) from Chinese Mg ingot suppliers, such as Taiyuan Yiwei Magnesium Industry Co. Ltd., (10 YiFen St., 9th Floor Suite 910, Taiyuan, Shanxi, 030024, China). Ultra-pure Mg ([Fe] ~ 2 ppm) may also soon be available from commercial Chinese Mg suppliers based on the research of Wang et al. [46].

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