MODELLING THE CORROSION OF MAGNESIUM AND ITS ALLOYS

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ABSTRACT
This study outlines the current approaches to the modelling of the corrosion of Mg and its alloys. The first part of the study describes the continuum damage models. In the latter part, a new model based on the corrosion chemistry is presented.

INTRODUCTION
Biodegradable materials have been extensively studied in recent years due to their potential to completely revolutionise the use of orthopaedic implants. Bone stability, essential during fracture healing, is usually achieved by implanting screws, plates and other fixing devices, which are removed after the bone has partially healed. Biodegradable implants are meant to gradually dissolve in human body, removing the need for a secondary surgery, as well as reducing other problems with permanent fixation devices, such as the stress shielding effect or inflammatory osteolysis [12].

In order for such bioimplants to be effective, it is vital for the material to maintain its mechanical integrity for long enough to allow the bone to regenerate [8]. It is therefore crucial to control the degradation rate of these materials.

One of the most promising elements when it comes to a design of biomaterials is Mg, on which we intend to focus in this review. The mechanical properties of Mg resemble these of a human bone [12], [15] and the chemistry of its degradation is relatively well-described in the literature. The corrosion of Mg consists of the following electrochemical reactions [13], [16]:

\[
\begin{align*}
Mg & \rightarrow Mg^{2+} + 2e^{-}, \\
2H_2O + 2e^- & \rightarrow H_2 + 2OH^-, \\
Mg^{2+} + 2OH^- & \rightarrow Mg(OH)_2.
\end{align*}
\]

Mg undergoes an anodic reaction (1) first. The emitted electrons then participate in a breaking of a water molecule in reaction (2). Reaction (3) is the formation of the main corrosion product, magnesium hydroxide Mg(OH)₂, which accumulates on the surface of the Mg matrix. It is important to note that one atom of Mg dissolved corresponds to exactly one particle of H₂ produced. Mg(OH)₂ has very low solubility in water, hence its layer on the Mg surface protects it from further degradation [9], [10], [14]. Presence of chloride ions Cl⁻ in human blood results in conversion of the magnesium hydroxide to magnesium chloride [5, 9], according to the following reaction:

\[
Mg(OH)_2 + 2Cl^- \rightarrow MgCl_2 + 2OH^-.
\]
MgCl₂ has much greater solubility in water than MgOH₂. Therefore MgCl₂ cannot provide an effective protection from corrosion and the magnesium matrix becomes exposed to the aggressive environment again [10].

The corrosion rate of Mg-based implants is a function of several factors: alloying and impurity contents, surface coatings and solution composition [5].

Corrosion of pure Mg and single-phase Mg alloys takes a form of a localised, irregular pitting, which then spreads laterally covering the whole exposed surface. Unlike in stainless steel, heavy pitting does not seem to be present. This is attributed to the fact, that the local increase in pH on the surface of the Mg matrix increases the stability of the protective Mg(OH)₂ film [10].

Presence of a beta phase in a Mg alloy is believed to have two effects on the corrosion behaviour. Firstly, in case of Al [10] and Rare Earth [2] alloys, the beta phase exhibits a passive corrosion behaviour. A continuous beta phase may therefore provide a barrier for corrosion. Secondly, the beta phase, having a more positive potential than Mg, serves as a cathode for microgalvanic corrosion, thus enhancing the corrosion rate [10].

A somehow less studied corrosion process occurring in Mg and its alloys is stress corrosion cracking (SCC). This complicated mechanism involves an enhanced corrosion rate due to the applied stress. A more detailed description of this process, involving a calculation of a stress threshold for SCC, is provided in [11].

In order to access the degradation rate of bioimplants, it is necessary to conduct very time-consuming experiments. The general practice involves immersing an Mg block in an aqueous environment simulating a body fluid and measuring the amount of hydrogen particles produced. A very accurate measurement system is described in detail in [7].

Because of the lengthy nature of these experiments, it would be beneficial to be able to preliminarily assess the degradation rate and ability to maintain mechanical integrity of an implant in silico. In this study, a current approach to such modelling is described and a new model for the corrosion is presented.

**MODELLING OF CORROSION**

The medical usage of bioimplants is a relatively new idea, which only recently has became mature enough to allow mathematical models to help with the design of such devices. Although some of the corrosion mechanisms, especially those taking place in Mg alloys, remain unclear, it is certainly possible to form basic models to numerically simulate the degradation.

**Continuum damage models**

Continuum damage (CD) models relate the microscopic discontinuities of the material to the changes in mechanical properties, such as stiffness or Young modulus [4]. By defining a scalar damage field $D$, which represents the loss of mechanical integrity due to degradation, an effective stress tensor $\tilde{\sigma}_{ij}$ is computed from the stress tensor $\sigma_{ij}$ according to:

$$\tilde{\sigma}_{ij} = \frac{\sigma_{ij}}{1 - D},$$

as described in [4]. The continuum damage model is then typically put in a Finite Element (FE) framework, where the damage scalar field is considered on an element by element basis. In order to capture various corrosion mechanisms, different evolution laws for $D$ are proposed in the literature.

**Scalar damage field $D$**

A model developed by Gastaldi et al. [4] decomposes $D$ into two parts by writing

$$D = D_U + D_{SC}.$$  

$D_U$ is assumed to evolve according to

$$\dot{D}_U = \frac{\delta_U}{L_c} k_U,$$
where $\delta_U$, $L_e$ are the characteristic lengths of respectively the element and the model and $k_U$ is a corrosion kinetic parameter.

Gastaldi et al. [4] assume that the damage field DSC evolves in the same manner as in stainless steel, as described by de Costa-Mattos et al. [3]:

$$D_{SC} = \frac{L_e}{\delta_{SC}} \left( \frac{S \sigma_{eq}^*}{1 - D} \right)^R,$$

(8)

when $\sigma_{eq}^* > \sigma_{th}$ and $D_{SC} = 0$ when $\sigma_{eq}^* \geq \sigma_{th}$. $L_e$ is as before, $\delta_{SC}$ is a characteristic dimension of the SC corrosion, $\sigma_{eq}^*$ is the equilibrium stress and $\sigma_{th}$ is the threshold stress below which the stress corrosion does not occur. $D$ is the total scalar damage field introduced in Equation (6). For a detailed discussion on the parameters please refer to [4].

A slightly different, purely phenomenological approach is used by Grogan et al. [5]. To model the heterogeneity of the corrosion, they adapted Equation (7) and proposed the following evolution law:

$$\dot{D}_U = \frac{\delta_U}{L_e} \lambda_U k_U,$$

(9)

where they introduced a pitting parameter $\lambda_U$ whose aim is to model the pitting behaviour. Initially, every FE exposed to the medium is given a random value of $\lambda_U$ sampled from a Weibull distribution with a probability density function

$$f(x) = \gamma x^{\gamma-1} \exp(-x^\gamma).$$

(10)

Higher values of $\gamma$ correspond to a more symmetric distribution, which in turn results in a more homogenous corrosion.

**Removal of the FE**

Once the value of a damage scalar field $D$ for an element reaches a certain threshold value (which varies from author to author), the element is removed from the mesh and the exposed corroding area is updated. In the model by Gastaldi et al. [4], the removal of an element results in its load being equally distributed among the neighbouring elements. In particular, this may trigger stress corrosion in one or more neighbours of the removed element.

The removal of elements in [5] results in the neighbouring elements inheriting the pitting parameter of the removed element. When an element is removed, its neighbours receive a new pitting parameter according to

$$\lambda_e = \beta \lambda_n,$$

(11)

where $\beta$ is a dimensionless positive parameter. High values of $\beta$ correspond to the material exhibiting heavy pitting corrosion.

**A model of the corrosion chemistry**

A common feature of the described models is a purely phenomenological approach to the microgalvanic corrosion. Although showing good agreement with the experiments, they provide little to understanding of the actual chemical processes occurring at the specimen-medium interface described in Introduction.

We are currently at the final stage of developing a model for the biodegradation of Mg and its alloys which bases on the knowledge about the chemical processes involved, which are described in Introduction [1]. In order to capture the complicated, evolving geometry of the specimen, the level-set method is used. The domain is divided into three subdomains: $\phi > 0$ (specimen), $\phi = 0$ (the interface) and $\phi < 0$ (medium). The level-set function $\phi$ evolves according to the level-set equation:

$$\frac{\partial \phi}{\partial t} + v |\nabla \phi| = 0,$$

(12)

where $v$ is the degradation velocity, which will be described in detail shortly.

We aim to model the concentrations of the main chemical species involved in the degradation – $Mg$ (magnesium inside the specimen), $Mg^{2+}$ (dissolved magnesium ions), chloride ions $Cl^-$
and the protective film $F$ (whose chemical composition depends on the alloy and the surrounding medium [14]). The model consisting of the following Partial Differential Equations (PDEs) is proposed, based on the chemical reactions (1)–(4):

\[
\frac{\partial [Mg]}{\partial t} = -k_1 [Mg] - k_2 [Mg], \\
\frac{\partial [Mg^{2+}]}{\partial t} = \nabla (D_{Mg^{2+}} \nabla [Mg^{2+}]) + k_1 [Mg] + k_3 F [Cl^-]^2, \\
\frac{\partial F}{\partial t} = k_2 [Mg] - k_3 F [Cl^-]^2, \\
\frac{\partial [Cl^-]}{\partial t} = \nabla (D_{Cl^-} \nabla [Cl^-]),
\]

where $k_1, k_2, k_3$ are the reaction rates and $D_{Mg^{2+}}$ and $D_{Cl^-}$ are the diffusion constants. To represent the closed environment of the in vitro experiments, $[Mg^{2+}]$ and $[Cl^-]$ are given zero-flux boundary conditions. It is important to note that the Equations (13) apply only to the part of the domain where $\phi < 0$ (i.e. the medium).

In order to take into account the protective effects of the corrosion products precipitating on the Mg surface, the following mechanism is implemented: once the protective film $F$ reaches a certain threshold $thresh$, it reduces the shrinking velocity $v$ in its neighbourhood so that:

\[
v(x, t) = \begin{cases} 
(1 - p)d, & \text{where dist}(x, \Omega_t) < r, \\
d, & \text{otherwise},
\end{cases}
\]

where $x$ is the position, $p$, which may take values between 0 and 1, is the protectiveness factor (which describes how protective the film is), $d$ is the base degradation rate and $\Omega_t$ is defined to be $\Omega_t = \{x: F(x, t) \geq thresh\}$.

Equation (14) is modified slightly when the model is applied to Mg alloys, in which the pitting corrosion dominates [10]. In case of rare earth alloys (which are most likely to be used in biomedical applications), the resulting beta-phase exhibits passive corrosion behaviour, so that the shrinkage velocity $v$ is set to 0 on the corresponding sites. This results in undermining and an eventual fall off of the beta particles.

For a certain choice of parameters, the above model correctly predicts the corrosion behaviour of an Mg sample – after a period of fast corrosion, a protective film forms on the sample surface which effectively inhibits the corrosion rate. This is consistent with the in-vitro experiments [9], [10].

Due to the lack of data on the reaction rates $k_1, k_2, k_3$ present in the model, as well as other parameters, a calibration procedure was required to estimate the parameter values. FreeFem++ [6] was used to solve the Equations (12) and (13). Data on the hydrogen evolution rate of High Purity Mg immersed in a Simulated Body Fluid from [7] was used. The results of this calibration are shown in Figure 1. For the exact values of the parameters, please refer to [1].

**DISCUSSION**

Although much progress was made in recent years in development of models for a degradation of Mg and its alloys, there is still a long way to go until such models become a useful tool in manufacturing bioimplants. In particular, being able to simulate their corrosion in silico facilitates the design of bioimplants with the required (often very specific) mechanical properties and the degradation rate below a prescribed threshold. As the corrosion behaviour of Mg and its alloys becomes understood better and better, it is necessary for the models to try to incorporate the subtle interplay between different alloy phases and impurities.
Careful quantification of the chemistry behind the corrosion may not only be used to make predictions about the corrosion behaviour, but may lead to revealing various interactions between different corrosion mechanisms.

The CD models described above are very convenient, as the corrosion contribution from different processes (microgalvanic, SCC) can be easily incorporated into the damage scalar field, for example by using linear superposition. The major drawback of the CD models described here is their phenomenological approach to microgalvanic corrosion – although making accurate predictions about the degradation rate is possible, the models do not aim to provide any further insight into the chemistry of the corrosion.

On the other hand, the PDE model outlined in this study is an attempt to model the chemical processes occurring on the scaffold-medium boundary. The data on the reaction rates is non-existent in the literature, therefore the model parameters \( k_1, k_2 \) and \( k_3 \) are only very roughly estimated. In order to model the corrosion rate more accurately, a series of dedicated experiments needs to be conducted. What is more, this model ignores other sources of corrosion, such as SCC.

Ideally, a combination of the two above approaches may provide an accurate description of the degradation mechanisms.

Corrosion of \( Mg \) and its alloys is a complicated electrochemical process. Mathematical modelling can be used not only to make predictions, but also to test theoretical hypotheses about mechanisms governing the corrosion. Further progress in this interdisciplinary field will require a strong cooperation between experimentalists and mathematicians.

In this study, CD corrosion models were described and some of their limitations were discussed. A new PDE model for the chemistry corrosion was developed and implemented. The PDE model was calibrated using the data on hydrogen evolution rate for a High Purity \( Mg \) immersed in a Simulated Body Fluid and is capable of simulating the degradation of Mg and its alloys. The PDE model, used either as a building block for the CD models or on its own, is believed to provide a useful framework for further modelling of the chemistry of corrosion.

REFERENCES


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