A Review of Models of Biodegradable Materials for Human Implantation of Medical Devices

Peyton O'Reilly[1*] and Inam UI Ahad [2]

[1] Department of Biomedical Engineering, The Ohio State University, Ohio, USA.
[2] Department of Mechanical and Manufacturing Engineering Dublin City University, Dublin Ireland
oreilly.160@buckeyemail.osu.edu

Abstract. The study of degradation and corrosion enable the development of corrosion resistant materials in many different usages specifically in the human body. Certain medical procedures and equipment need placement of biodegradable materials such as the placement of a stent. Magnesium based alloys biodegrade within the human body making them a viable material in medicine. Magnesium based alloys have a fast degradation rate which can affect the healing process. This paper is a literature review to address the concerns of degradation rates of biodegradable materials based on models to understand degradation rates, hydrogen absorption and desorption, pourbaix diagrams, and corrosion, and reactions.

Keywords: Degradation, Models, Alloy

1 Introduction

1.1 Pourbaix Diagrams

Pourbaix diagrams demonstrates the regions of electrochemical stability of different metals and mineral phases regarding pH and electrical potential. However, the diagram cannot provide information about the corrosion reactions that can and may occur [1]. Pourbaix diagram should act as a basis for corrosion data, as it has limitations especially in water [2].

1.2 Degradation Rate

Magnesium based alloys have a fast degradation rate and are biodegradable materials in the body. However, the alloys degradation rate should be equal to the time the tissues recover after placement of material in the body. Magnesium based alloy with respect to clinical application can affect the healing process, and the mechanical properties of the alloy. To slow the degradation rate, the corrosion mechanism must be analyzed. Previous models have focused on corrosion models at a qualitative level. However, qualitative models cannot be applied as an engineering or orthopedic application [3].
Hydrogen absorption enhances material development. To understand H_2 and metal interactions, the study of kinetics of hydrogen absorption and desorption must occur

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[4]. For the study of corrosion reaction, specifically the alloy magnesium electrochemical corrosion, hydrogen evaluation reaction (HER) should be studied.

Corrosion rate data is useful to engineers when designing materials, including biodegradable, with minimal alteration to the mechanical properties. As decrease in grain size decreases the corrosion rate, an equation can be used to model degradation rate data [5]. This equation is specific with grain size but is not for material dependent properties.

$$CR = CR_0 + b \times f_{a,m} \times D^{-0.5} + c \times \sum(f_{A,i} \times |\Delta E| \quad (1)$$

Table 1. Symbol Description of Degradation Rate equation

Symbols	Meaning
CR	Degradation Rate
CR_0	Matrix Surface Energy
b	Intrinsic and Extrinsic effects of grain size relative to degradation solution
$f_{A,m}$	Surface Fraction
D	Grain size
c	Contributions of the second phase
$f_{A,i}$	Area fraction of the second phase
ΔE	Volta potential difference of cathodic and anodic second phase

2 Methods and Applications

2.1 Hydrogen Adsorption

The Johnson-Mehl-Arvami-Kolmogorov (JMAK) models nucleation, and growth for hydrogen adsorption kinetics [5]. JMAK has been used to predict the alloy's solid-state transformation when thermodynamics impact is held constant. A study was conducted that focused on hydride sorption at various temperatures and pressure. Upon the hydrogen absorption experiments, time domain simulations, and data processing was conducted with MATLAB (self-programmed). Pressure Composition temperatures (PCT) were conducted with the sample; this data developed the PCT model to identify H_2 equilibrium content at any point in time [4]. k

2.2 Hydrogen Evaluation Reaction (HER)

To model HER, the three mechanisms, the Volmer, Tafel and Heyrovsky were considered. The mechanisms are the rate determining steps of HER. The Volmer step describes the electrode and the potential of the current passing through in the electrochemical system. Whereas the Tafel equation is the relation of the overpotential to the electrochemical reaction and focuses on the catalyst's active site. The Heyrovsky

reaction focuses on producing H_2 [6]. Based on the models, when all the mechanisms are the rate determining step, the current density of HER is dependent on Gibbs Free Energy with respect to orientation, alloying and surface defects. Computational testing was conducted to validate the model. This model validated and has proven the connection between overpotential of HER and the hydrogen evaluation rate [7].

2.3 Models of Biodegradable Alloys

To ensure safe biodegradable medical equipment for patients, models must be considered to understand degradation rate of alloys. With certain parameters, the models can alter the speed of the degradation rate. With the right materials and degradation rate, biodegradable promote tissue regeneration and healing of the body after implantation. Mg alloys degradation rate can be too fast which can hinder the mechanical integrity due to hydrogen gas generation [8]. The compromised mechanical integrity of the alloy can alter the healing process. To eliminate the challenges of biodegradable materials, models of degradation rates have been developed to measure and decelerate the rate. The following Table 2 gives analysis of biodegradation models in other works developed to, measure, understand and slow degradation rate.

Table 2. Summary of Biodegradation Models

Alloy System	Biodegradation Model	Input and Output Parameters	Units	Ref.
Fe - inhibitors	Density functional theory (DFT) – computational model	HUMO, LUMO, HOMO-LUMO energy gap, dipole moment.	eV	[9]
Fe inhibitor	Molecular Dynamics Simulation (MD) – computational model	Input – Interaction energy Output – Absorption energy of metal inhibitor interactions	$E_{ads} - kJmol{-}1$	[9]
Al inhibitors	DFT computational model	Input – coumarin molecules Output – energy levels	eV	[9]
Al inhibitors	MD computational model	Input – aqueous layer and Al (111) Output – RDF curve of Al	Å (radius A)	[9]
Cu inhibitors	DFT and Reactive force field (ReaxFF) – computational model	Output – Bond order, bond length, interaction energy	eV	[9]

Cu inhibitor	MD computational model	Input – 200 H_2O, 3 Na^+, 3 Cl^-, Cu (111) Output – Bond length	Å (radius A)	[9]
Fe14Cr8Mn alloy	DFT computational model	Input – calculated chemical indices	eV	[10]
Fe – 14Cr8Mn alloy	Monte Carlo Simulation	Output- energies for adsorption of histidine, tryptophan, and tyrosine	Kcal/mol	[10]
		Total Energy,	Kcal/mol	
		Adsorption Energy, Rigid Adsorption Energy, Deformation Energy	Kcal/mol	
		Inhibitor and water	(dE_{ads}/dNi) $(kcal/mol)$	
Mg alloy	Degradation mathematical model	Input parameters – composition, grain size, and precipitations	V/s	[5]
Mg alloy	Diffusion based mathematical model	Input – Fick's Law, composition of degradation medium, absent corrosion layer Output – concentration of degradation layer	m^2/s	[3]
Mg-1Ca Mg-3Ge	Finite element simulation – computational home	Parameters depend on the material used; basic parameters include: $\rho_{Mg}(kg/m^3)$ $p_{Mg(OH)_2}(kg/m^3)$ $\rho_{H2}(kg/m^3)$ $C_{Hanks}(mol/L)$ $a(mm)$ $M_{Mg}(g/mol)$	mm^2/h	[3]

Mg alloy	Degradation rate prediction - machine learning model	Parameters depend on the four algorithms: E_{corr}: I_{corr} RF : n_estimators =150, n_estimators =183 SVR: Kernel =rbf, C =100, gramma = 0.1 XGBoost: Booster=gbtree, learning_rate =0.2 n_estimators =10	Unitless – prediction accuracy	[11]
Mg- Zn alloy	Pourbaix Diagram – ab initio approach	Input – Energy and chemical potential calculations Output – E and pH to formulate ΔG and calculation of vertices	Volts	[12]

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Compared to copper, iron and aluminum-based alloys, magnesium-based alloys have a faster degradation rate. Zinc is a favorable alloy due to its degradation time in comparison to Fe and Mg[13]. However, the mechanical properties of Zn are weaker than Mg and Fe. Fe ,Cu and Al [13]inhibitors were modeled with both the density functional theory (DFT) and the molecular dynamics simulation. Density functional theory (DFT) is a quantum modeling technology system to understand the highest and lowest occupied molecular orbital (HOMO and LUMO), as well as a change in energy [9]. These parameters are used in relation to degradation inhibitor alloys. Molecular dynamics (MD) uses interaction energy to understand unshared electrons on the alloy surface and the bond interactions. MD enables analysis of the relation of the structure of the alloy and the corrosion inhibition [9].

With the machine learning model, degradation potential, chemical and degradation of magnesium alloy can be predicted. Degradation potential and current density was measured in regard to the four algorithms: RF, MLR, SVR and XGBoost algorithms [11]. A new simulation of Pourbaix diagram was developed for Mg – Zn alloy in Cl solutions to further monitor degradation behaviors of the alloy. With the new Pourbaix simulation, the degradation behavior of the Mg – Zn alloy was able to be analyzed.

3 Conclusion

Computational model, mathematical modeling, and Pourbaix diagrams have potential for controlling and slowing corrosion and degradation rates. Machine learning algorithms can further knowledge about prediction of degradation rate. Limitations of biodegradable materials include the possibility of the inability to properly breakdown in the body. By strengthening mechanical properties of Zn or focusing on the degradation rate of Mg, further research will prevent long term complications of stent implantation. By understanding corrosion and degradation, the degradation rate of magnesium-based alloy and alloy inhibitors can be controlled and enhanced for clinical application.

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