MATERIALS PROCESSING AND CARACTERIZATION IN BIODEGRADABLE

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Submission date: 17-Nov-2020 04:28PM (UTC+0800)
Submission ID: 1448801677
File name: NG_AND_CARACTERIZATION_IN_BIODEGRADABLE_IMPLANTS_DEVELOPMENT.pdf (4.11M)
Word count: 6409
Character count: 35910

Materials : Technology and Applications Series 1
ISBN 978-967-2389-09-5
2019

CHAPTER 4

MATERIALS PROCESSING AND CARACTERIZATION IN BIODEGRADABLE IMPLANTS DEVELOPMENT

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4.1 INTRODUCTION

Current metal biomaterials for biomedical applications tend to use a lot of prosthetic devices (prosthetic devices) to help, repair and regeneration of damaged tissue. Metallic biomaterials can be used as a permanent function or temporary functions. However, metal biomaterials is still in need of repairs and improvements in biocompatibility and biofunctionality [1]. Several researches conducted to study the behavior of metallic implants in order to improve the biocompatibility in the last few years [2, 3]. Recent studies on the in vivo have shown that metal ions and particles are separated due to the friction of the implant that can cause damage to the soft tissue [4]. General agreement that the important factors affecting the longevity of orthopedic implants are the release of

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metal ions from the implant [4-6], formation of debris associated with the problem of tissue inflammation, bone loss and loosened implant [7]. Therefore, efforts should be made is the improvement of the mechanical properties.

In titanium (Ti) and its alloys have been carried out efforts to improve the mechanical properties by controlling processing conditions [8]. The processing is done by the application of treatment and the addition of numbers of elements [1, 9-13]. Some of the treatment given to the Ti alloy can change its properties such as texture control, heat treatment (aging) as well as combination deformation-heat treatment [1, 11]. The deformation process often given in Ti alloys includes equal channel angular pressing (ECAP), accumulative roll bonding (ARB) and high pressure torsion (HPT) [1]. Table 4.1 showing the effect of elements on titanium (Ti) and its alloys which gives an effect on the cost production and ease of implant is removed.

Table 4.1: Selection of titanium (Ti) and its alloys based on the consumption of the elements against the cost (high and low) and removable implants [1]

Ti alloys with consumption of high cost elements	Ti alloys with consumption of low cost elements	Ti alloys for removable implants
Ti–13Nb–13Zr	Ti–10Cr–Al	Ti–Zr–Nb
Ti–12Mo–6Zr–2Fe (TMZF) (ASTM F1813)	Ti–Mn–Fe	Ti–Zr–Nb–Ta
Ti–15Mo (ASTM F2066)	Ti–Mn–Al	Ti–Zr–Al–V
Ti–16Nb–10Hf (Tiadyne 1610)	Ti–Cr–Al	Ti–30Zr–5Mo
Ti–15Mo–5Zr–3Al	Ti–Sn–Cr	Ti–30Zr–7Mo
Ti–35.5Nb–7.1Zr–5.1Ta (TNZT)	Ti–Cr–Sn-Zr	Ti–30Zr–5Cr
Ti–29Nb–13Ta-4.6Zr (TNTZ)	Ti–(Cr, Mn)–Sn	Ti–30Zr–3Cr–3Mo
Ti–Nb–In	Ti–12Cr	
Ti–24Nb–4Zr-7.9Sn (Ti2448)		
Ti–Cr–Sn-Zr		
Ti–Zr-Cr		
Ti–Zr-Mo		
Ti–Zr-Mo-Cr		

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4.2 BIODEGRADABLE METALS

4.2.1 Definition and Concept of Biodegradable Metals

The term "biodegradable metal" (BM) has been used worldwide and there were many new findings reported over the last decade [14]. Hopefully, the advent of this new implant materials can support the healing process of diseased tissue or organ and subsequently degraded slowly [15]. Definition of biodegradable metals (BMs) according to Li, Zheng et al. 2014 is a metals that were expected to corrode in vivo, where the corrosion products of metals provide response corresponding to the "host" and dissolve completely upon fulfilling the mission to assist the tissue healing with no implant residues [16].
From the point of view of materials science, biodegradable metals can be classified as follows: [14]

- **"Pure metals" (BMs-PM)** is a metal with one metallic element with impurity levels lower than the commercial tolerance limits.
- **"Biodegradable alloys" (BMs-BA)** is a metal with various microstructures and one or more alloying elements.
- **"Biodegradable metal matrix composites" (BMs-MC)** is all the components forming biodegradable composites have a category of the materials are non-toxic to the body.

Li, Zheng et al. 2014 said the development of new materials along with the improvement of living standards and expectations of quality of life [16]. In other clinical applications only require temporary support to the healing process of tissue [16], therefore, required new materials. Such support is only derived from material made of degradable biomaterials [15, 17]. Biodegradable concept has long been known, for example in biodegradable polymer sutures [16]. There are two degradable biomaterial implants that have been proposed: biodegradable polymers and biodegradable metals [15]. However, biodegradable polymers have biomechanical limitation compared to biodegradable metals [18]. On the other hand, biodegradable metals have both the strength and the ability to degrade [19]. During the past several years, biodegradable metals were used as a temporary implant material for vascular intervention and osteosynthesis [20-26].

4.2.2 Magnesium-based biodegradable metals

When viewed from the alloying elements, there are three major groups of magnesium alloys including pure magnesium (pure Mg), magnesium alloys with the main alloying elements Al and alloys magnesium free of alloying elements Al [27-30].

4.2.3 Pure magnesium

Pure magnesium is magnesium with other elements (impurities) within tolerance limit. If impurities exceed the tolerance limit, the corrosion rate will increase [31, 32]. The corrosion resistance of pure magnesium is higher by improving the grain size through forging or rolling and heat treatment [32]. The heating temperature and the length of time of the heat treatment must be considered properly. Otherwise, it would get the opposite result [32].

Therefore pure magnesium demonstrated the ability to stimulate new bone formation, Huang, Ren et al and Gao, Qiao et al still worrying about its mechanical properties in orthopedic applications [33, 34]. Li and Zheng said that the pure magnesium is not the right material for biodegradable vascular stents [32].

4.2.4 Magnesium alloys with the main alloying elements Al

Types of magnesium alloys containing elements of Al are AZ91, AZ31, AE21, Calcium (Ca) modified AZ alloys and AE42 [35, 36]. LAE442 alloy is the development of magnesium alloys (AE42) with low density but it will increase the ductility and corrosion resistance [37].

Additional of Mn increase the ductility and corrosion control with bind Fe (adverse effect from Fe on the corrosion behavior) [30]. Addition of Zn can form a solid solution strengthening [35] to increase strength and castability [30]. However, when combined with Al larger (> 2wt.%) it result in embrittlement [36]. Other alloying elements in magnesium alloys containing Al is Lithium. Lithium has unique properties which are able to change the lattice structure of the HCP into BCC in magnesium alloys [38].

4.2.5 Free-Al Magnesium alloy

Magnesium alloys with free-Al are WE, MZ, WZ and Mg–Ca alloys [30]. The addition of some elements such as Yttrium (Y), zirconium (Zr), Zinc (Zn) and RE almost certain to improve the properties (creep resistance, high temperature stability and forgingability) of the alloy in transportation industry applications [35, 36].

4.2.6 Iron-based biodegradable metals

Pure Fe and Fe based alloys have been developed as biodegradable metals other than Mg and Mg based alloys [1]. From the point of view of structure, Mg and Mg based alloys do not always meet the mechanical properties while pure Fe and Fe based alloys have higher strength [1, 39, 40]. Pure Fe and Fe based alloys are considered as candidate to be used as an alternative to biodegradable implant material [26, 41-44].

The results of pure Fe in vivo tests showed no toxicity [45]. But the results of in vitro showed the concentration of iron ions in the body should not be more than 50 µg/ml because it will cause toxicity and cell death [44, 46]. One thing to note is the excessive degradation after implantation of pure iron at the organism. This is because it is dangerous for the healing of wounds, especially in the early stages of operation [42, 47].

4.3 MATERIALS PROCESSING

Currently, processing material reliable cannot be separated from the increased mechanical properties, alloy design advances (the influence of alloying elements) and process optimization [8, 48]. Magnesium and its alloys still have some issues that should be considered as limited mechanical properties and the problems with low corrosion resistance [49]. Attempts have been made regarding the development of magnesium and its alloys by reducing and controlling the corrosion rate and maintaining biocompatibility [49]. Generally, there are two ways to improve the corrosion behavior of magnesium and its alloys: (a) adjusting the composition and microstructure, including grain size [29, 50] and texture [51] from base material (not only of alloys) [52], but through development of optimal methods of production and availability of raw materials [53]; (b) conducting a surface treatment or coating [54] such as using ceramic, polymer or composite layer [49].

Arrangements the chemical composition of Mg and its alloys has been carried out since 1990 for transportation applications and recent years, particular researchers of biomaterials were interested in developing a variety of medical devices made from Magnesium alloys [20, 28, 55-66].

The corrosion resistance of pure magnesium is higher by improving the grain size through forging or rolling and heat treatment [32]. As for magnesium alloys with main alloying element Al commonly formed complex compounds to solid solution strengthening, precipitation strengthening and grain-boundaries strengthening [30]. The addition of the element Rare earths (RE) in the magnesium alloys with main alloying element Al and magnesium alloys with free-Al have several contributions such as strengthening, raising the creep resistance, increasing corrosion resistance [67], forgingability [35, 36] and all efforts made to improve services Mg alloys in the transportation industry [35, 36, 67]. Based on research, recommended types magnesium alloys used for biomedical use in human is magnesium alloys free-Al without harmful elements such as RE [68]. Therefore, good alloys element candidates to be used in biomedical magnesium alloys include Ca, Mn and Zn [63, 69, 70].

While efforts were made to pure Fe and Fe based alloys is to increase the degradation rate is still very low and considered to have the same reaction with a permanent implant [42, 71]. Development of research results of pure Fe and Fe based alloys is still of concern to such as the attainment of the level of degradation, mechanical performance and maintaining biocompatibility [71]. To get the appropriate design, there are several things that must be considered like manufacturing process, selection of elements alloys [39, 42, 45] and heat treatment to control the grain size [1, 39, 72].

For other biodegradable metals such as Zn a metallic element that is important and second most widely found in the human body [73]. Currently, Zinc is used as an alloying element, especially in biodegradable metal Mg-based [16]. Efforts made to alter the mechanical properties of pure Zn by adding alloying elements and adjustment microstructure through mechanical deformation [16]. The mechanical deformation effective to improve the mechanical properties and corrosion properties of biodegradable metal are rolling (hot/cold), extrusion, equal-channel angular pressing (ECAP), high pressure torsion (HPT), drawing and forging can be seen in Figure 4.1 [14, 57, 74].

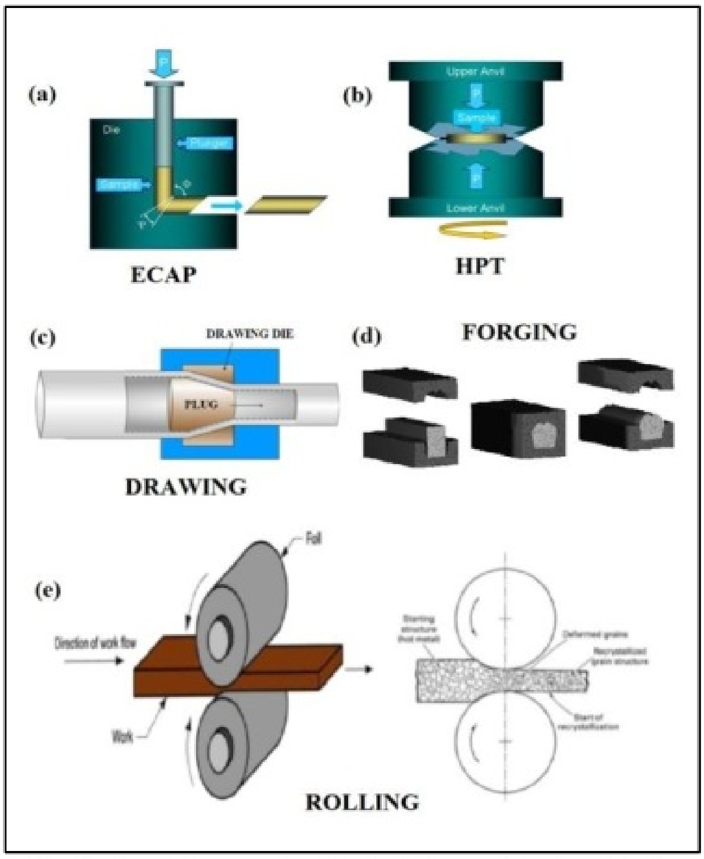

Figure 4.1: Schematic mechanical deformation for biodegradable metals

Materials processing can be selected based on specific application [75]. An example is the friction welding process. Nasution, Murni et al. 2014 has done a friction welding between pure Fe (biodegradable metal) and SS316L (inert metal) for treating temporary clinical problems such as bone fracture [76]. Friction welding has a number of advantages such as low heat input, narrow heat-affected zone (HAZ), and low residual stresses [76] and distortion [75-77]. The results of the connection of welding dissimilar materials can be seen in Figure 4.2.

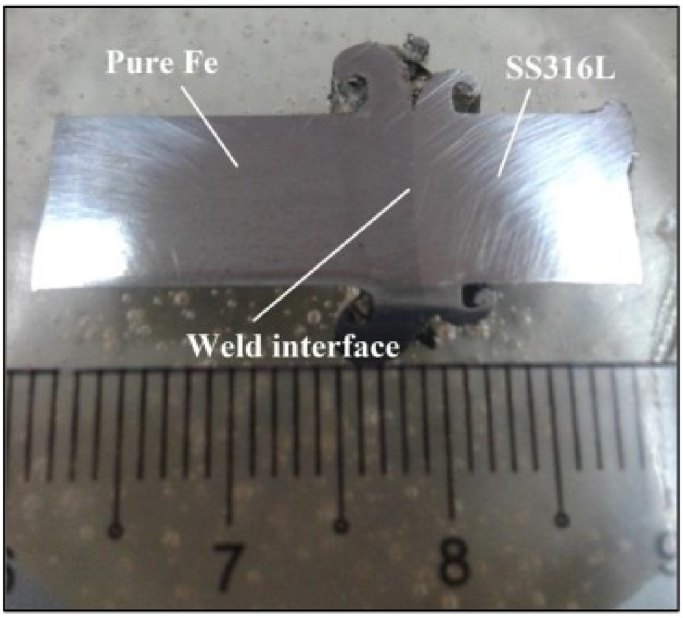

Figure 4.2: Dissimilar metals were joined through the friction welding

4.4 CHARACTERIZATION

4.4.1 Potentiodynamic polarization test (PDP)

The most commonly used technique to evaluate the degradation behaviour of the biodegradable metallic implants is potentiodynamic polarization test. The PDP plays a vital role in determining and quantifying the mechanistic corrosion of the biodegradable metals in simulated body fluid (SBF). An external voltage is applied by a potentiostat and the corresponding current density on the working electrode (samples) is monitored. 3-electrodes set up are often used in the test comprising of a reference electrode (Ag/AgCl, saturated Calomel), an auxiliary electrode (Graphite, Platinum) and a working electrode (tested samples). The reference electrode is used to measure the working electrode potential. A reference electrode should have a constant electrochemical potential as long as no current flows through it. The auxiliary/counter electrode functions to provide a complete circuit allowing current to flow between the working electrode [78]. Figure 4.3 shows the 3-electrodes configuration for the PDP test in estimating the corrosion rate of the biodegradable metals.

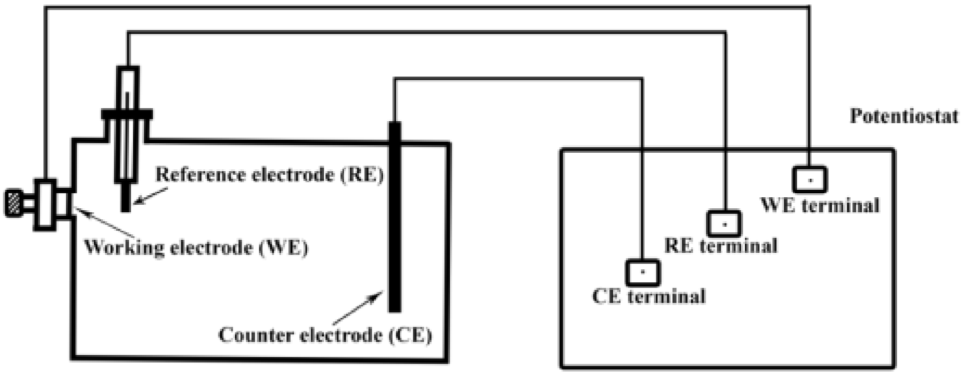

Figure 4.3: 3-electrodes set-up for the potentiodynamic polarization test

4.4.1.1 Interpretation of the PDP curves

The PDP curves could provide a quantitative interpretation on the corrosion rate of the different samples, as shown in Figure 4.4. Qualitatively, from the Figure 4, corrosion rate of sample A is higher than that of sample B and sample C in the order of sample A > sample B > sample C, as the curve of sample A resides at the rightmost indicating the highest current density, i_{corr}. Current density measures the electrical current flowing through the exposed area of the working electrode.

Tafel slopes are constructed on both the anodic and cathodic branches of the polarization curves and the slopes can be extrapolated back to the open-circuit corrosion potential to give a corrosion current density. Quantitatively, the current density of the sample A, sample B and sample C are about 6.9 x 10-6, 2.3 x 10-6, and 6 x 10-7 A/cm2, respectively, determined by the Tafel extrapolation method. The corrosion rate is directly proportional to the current density.

Through the PDP curve as well, the corrosion potential E_{corr} can be quantified. It is a potential at which the rate of oxidation is exactly equal to the rate of reduction. At this potential, the anodic currents and cathodic currents are equal in magnitude and hence no net current could be measured. At this potential, all electrons generated by oxidation metal in dissolution reaction are consumed by oxidant reduction reaction on the same metal surface.

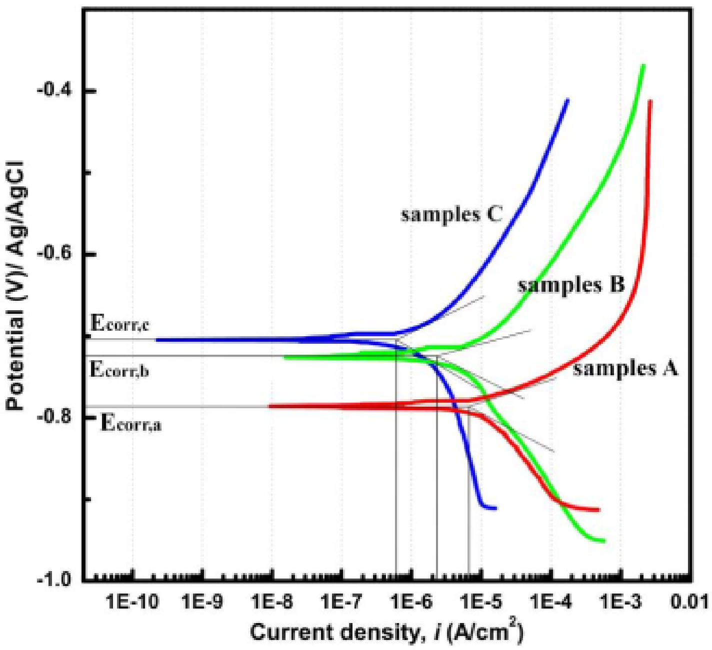

Figure 4.4 Determination of corrosion potential and corrosion current density through Tafel extrapolation technique.

The corrosion current density determined from the Tafel extrapolation method then will be used to calculate the corrosion rate of the corroding metals. Based on the ASTM G59−97 (2014), the corrosion rate can be estimated by the following expression

$$CR = 3.27\ x\ 10^3 . \frac{i_{corr}}{\rho} EW$$

where i_{corr}= corrosion current density (μA/cm2), EW = equivalent weight and ρ = density.

ASTM G59 – 97 (2014) and ASTM G5 – 14 are utilized as the guidance to conduct the PDP test and to analyse the results obtained

The quantification of the corrosion rates of the biodegradable metals in the implant application researches is an indispensable aspect since the degradation rate should be monitored over the implantation period so as it tailors with the tissue healing time [79]. In many biodegradation studies, the corrosion rates of pure Fe, pure Mg, Fe-based alloys and Mg-based alloys have been determined by the PDP test through the Tafel extrapolation method [80-83]

4.4.2 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy is one of the vital techniques in characterizing the corrosion behaviour of the biodegradable metals, particularly for the coated metals. In EIS, the frequency is applied by the potentiostat and the corresponding impedances are obtained.

In recent years, EIS have been of great interests in the study of corrosion system whereby it has been used effectively to measure the polarization resistance for corrosion systems. It is very useful in order to characterize a coated metal substrate by analysing two occurrences: (1) the deterioration of the coating due to electrolyte exposure (2) the increase or change in corrosion rate of the underlying substrate due to the deterioration or delamination of the coating and subsequent attack by the electrolyte. In EIS, the electrochemical interaction at electrode - electrolyte interface can be characterized by an analogous electronic equivalent circuit consisting of a specific combination of resistors and capacitor. The equivalent circuits are constructed after getting the data of applied frequencies (f), imaginary impedances (Zi), real impedances (Zreal), absolute impedances (|Z|) and phase angles (θ) with the aid of special software. Simply speaking, an equivalent circuit transforms the frequency response data to corrosion properties in terms of resistance and impedance.

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Nyquist plot gives the plot of the real part of impedance against the imaginary part. This plot gives a quick overview of the data and provides some qualitative interpretations from the shape of the curves. Another plot, called Bode plot indicates the absolute impedances, |Z| and the phase angles, θ of the impedances, each as a function of frequency. Figure 4.5 shows the typical equivalent circuit of an organic coating on a metal substrate.

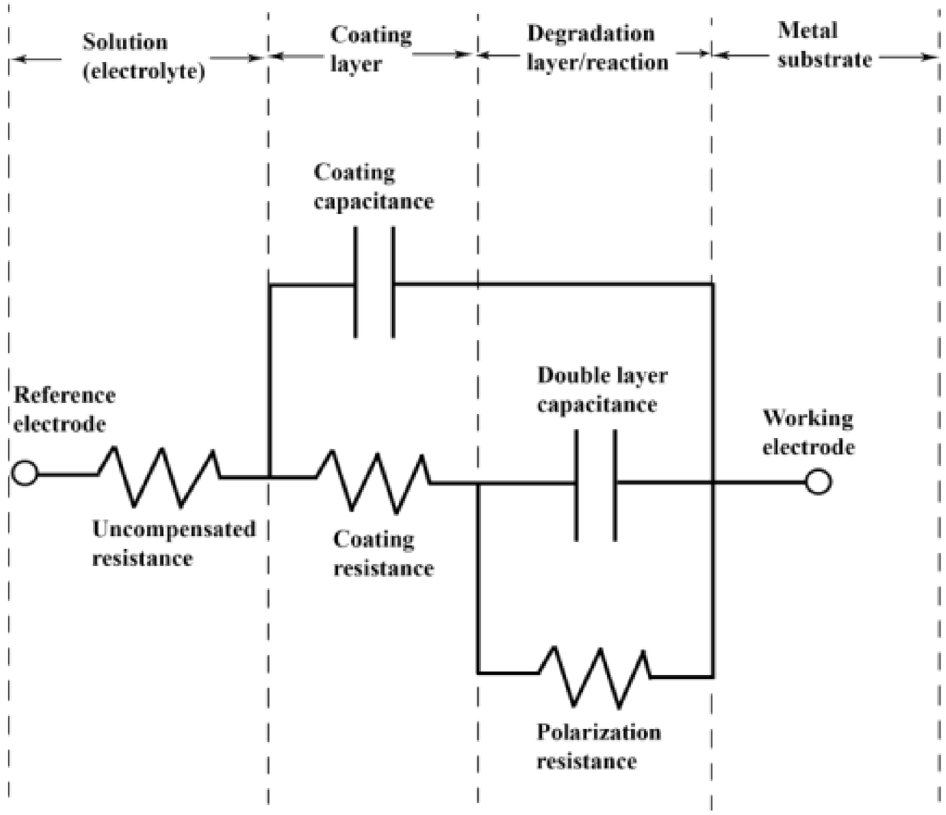

Figure 4.5 Typical equivalent circuit of a coated metal

It is noteworthy to define some important parameters in the EIS.

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a) Ohmic resistance (RΩ)

Ohmic resistance or so-called uncompensated resistance is the potential drop between the reference electrode and the working electrode. It depends on the conductivity of the electrolyte and the geometry of the electrode as well.

b) Pore resistance, Rpo

Rpo is a resistance developed by the organic coating. It may indicate the coating's porosity as the resistance will decrease once the coating experienced an increase of porosity.

c) Polarization resistance, Rp

The corrosion rate of the metal substrate beneath the coating can be interpreted by the Rp. High Rp of a metal implies high corrosion resistance. The value of Rp can be estimated through the equivalent circuit modelled.

d) Coating capacitance, CC

The Cc is an important parameter in analysing the coating failure. For polymer-coated metal, the coating capacitance is given by:

$$Cc = \frac{\varepsilon\varepsilon_0}{d} A$$

Where, ε is the dielectric constant of the coating, ε0 is the dielectric constant of vacuum, A is the area of the coating, d is the thickness of the coating. When water penetrates the coating, its dielectric constant increases, leading to an increase of coating capacitance. Hence, the coating capacitance can be utilized to measure the water uptake by the coating.

e) Double layer capacitance, Cdl

Cdl is the capacitance at which the corrosion reaction takes place. It may indicate the delamination or deterioration of the coating.

f) Constant Phase Element, CPE

In some cases, CPE is used in replacing the capacitance considering the deviation from ideal capacitor behaviour owing to the certain heterogeneity of the electrode surfaces.

$$CPE = \frac{1}{Y_0(j\omega)^n}$$

where, Y_0 is the admittance of an ideal capacitance and n is an empirical constant, ranging from 0 to 1. When n= 1, the CPE behaves as a pure capacitor, while when n= 0, the CPE behaves a pure resistor.

g) Warburg Impedance, W

The diffusion of ionic species at the metal-electrolyte interface is modelled by the Warburg impedance. Warburg impedance is characterized by having identical real and imaginary contributions, resulting in a phase angle of 45° in a Bode plot. The Warburg impedance is determined by the following expression;

$$W = \frac{1}{Y_0\sqrt{j\omega}}$$

where, Y_0 is the diffusion admittance.

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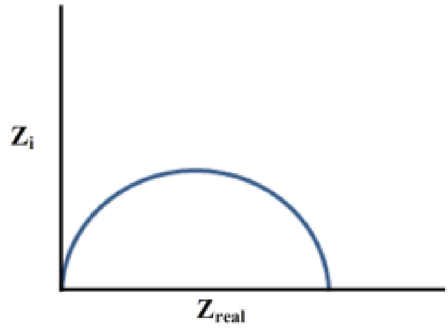
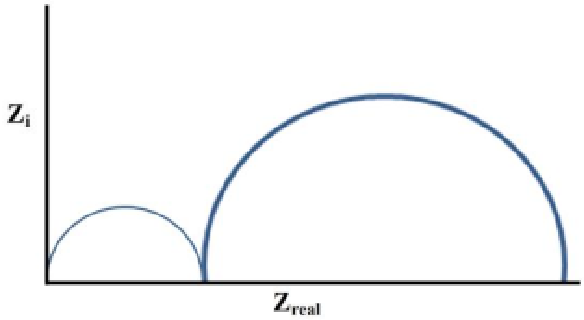
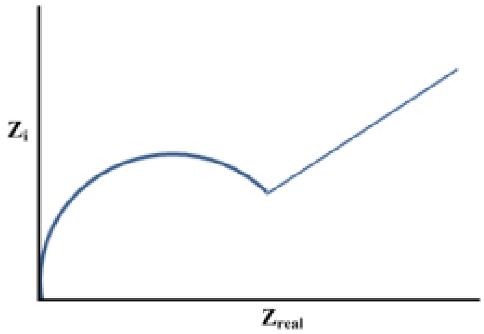
Table 4.2: Shows typical Nyquist plots in the case of organic coated-metal being immersed in an electrolyte indicating the electrochemical interaction at metal-electrolyte interface.

Nyquist plots	Description
	• Development of a low pore resistance, R_{po} • Penetrating of the electrolyte via the pore channel to the surface of the underlying metal.
	• Two impedance loops • First smaller loop indicates coating capacitance C_C and second loop postulates double layer capacitance C_{dl}
	• Warburg impedance indicated by the 45°- slope line. • Diffusion of the electrolyte ionic species on the metal surfaces.

There have been intense uses of the EIS in studying the corrosion behaviour of the biodegradable metals particularly of the coated metals. An EIS study has been conducted on PLA coated- AZ91 magnesium alloy samples. The degradation resistance created by the PLA coating were evaluated by examining the changes in the Nyquist plots at predetermined time intervals [84]. Another EIS study by Zomorodian et al. employed a composite coating comprising of polyether imide PEI, diethylene triamine and hydroxyapatite applied on AZ31 magnesium alloys. The coating performance was evaluated using EIS technique for 88 days by analysing the changes in the absolute impedances, |Z| and the phase angles, θ of the impedances through the Bode plots [85]. Very recently, both Nyquist plot and Bode plot have been analysed in an EIS study to investigate the degradation behaviour of Fe-Au and Fe-Ag composite biodegradable stents [83].

4.5 CONCLUSION

This chapter has presented a brief report on material processing and characterization in the development of current biodegradable implants. Although this chapter is intended as an a preliminary introduction to the processing of materials and the characterization of biodegradable implants includes the measurement and determination of the corrosion rate of biodegradable implants. Measurement and determination of corrosion rates using potentiodynamic polarization tests and electrochemical impedance spectroscopy are currently widely used by researchers in the field of biomaterials.

ACKNOWLEDGEMENT

This work was supported the Ministries of Research, Technology, And Higher Education Republic of Indonesia through Director of Research and Community Service with contract number: 009/L10/AK.04/KONTRAK-PENELITIAN/2019. Apart from that, This work was financially supported by the Universiti Teknologi Malaysia under the Research University Grant (20H20, 4J358, 15J84 and 20H26), Ministry of Energy, Science, Technology, Environment and Climate Change (EF0618I1166 and 4S144) Fundamental Research Grant Scheme (FRGS) Ministry of Education Malaysia (278784-294883).

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