TITANIUM DIOXIDE (TiO2) SOL GEL COATING ON 316L STAINLESS STEEL

NORHASLINA ABDUL AZIZ

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Faculty of Mechanical and Manufacturing Engineering
Universiti Tun Hussein Onn Malaysia

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The work presented in this thesis deals with experimental and theoretical studies related to titanium dioxide (TiO$_2$) thin films. The main purpose of this research is to prepare the TiO$_2$ sol gel coating on 316L stainless steel with the effect of withdrawal speed and heat treatment. The whole project is emphasis on composition of TiO$_2$ coating on 316L stainless steel and how it affected by the different withdrawal speed and heat treatment temperature. The parameters used in this study are calcination temperature (300°C, 500°C and 700°C) and withdrawal speed (6mm/min, 30mm/min and 60mm/min). The coatings were obtained by the sol-gel method. Titanium (IV) butoxide was used as a TiO$_2$ precursor in the sol gel process. Stainless steel 316L was coated with dip coating method. In this experiment, the characteristics of the TiO$_2$ sol-gel coating on 316L stainless steel were investigated using Fourier transform infrared spectroscopy (FTIR) for structural/bonding determination, X-ray diffraction (XRD) for phase determination and Scanning electron microscopy (SEM) for morphology of the sample. Then, corrosion behavior of the sample was obtained by electrochemistry test. The coating was examined in 3.5% NaCl at room temperature (25±0.2°C). In the solution examined, anatase crystallite exist at calcined temperature 500°C while rutile crystallite at 700°C. The value of corrosion rate increased as the calcined temperature increased and the best protective properties exhibit at 300°C and withdrawal speed 60 mm/min. The result shows that as calcined temperature increased, the corrosion rate increased and the corrosion current density decreased gradually. Other than that, as the withdrawal speed increased, the films particles become more compact and also the grain size become more distinct.
ABSTRAK

Kajian yang dibentangkan di dalam tesis ini adalah berkenaan dengan eksperimen dan teori yang berkaitan dengan filem nipis titanium dioksida (TiO₂). Tujuan utama kajian ini adalah untuk menyediakan salutan sol gel TiO₂ pada 316L keluli tahan karat dengan kajian kelajuan pengeluaran dan rawatan haba. Keseluruhan kajian ini menunjukkan komposisi lapisan salutan TiO₂ pada 316L keluli tahan karat dan bagaimana ia dipengaruhi oleh kelajuan pengeluaran dan rawatan haba pada suhu yang berbeza. Parameter yang digunakan dalam kajian ini adalah suhu pengkalsinan (300°C, 500°C dan 700°C) serta kelajuan pengeluaran (6mm/min, 30mm/min dan 60mm/min). Lapisan diperolehi dengan kaedah sol-gel. Titanium (IV) butoxide digunakan sebagai pelopor TiO₂ dalam proses sol gel. Keluli tahan karat 316L telah disalut dengan kaedah salutan celup. Dalam eksperimen ini, ciri-ciri lapisan sol-gel TiO₂ pada 316L keluli tahan karat telah diperoleh menggunakan spektroskopi inframerah transformasi Fourier (FTIR) untuk penentuan struktur / ikatan, pembelauan sinar-X (XRD) untuk penentuan fasa dan mikroskop imbasan elektron (SEM) untuk morfologi sampel. Kemudian, kakisan sampel itu didapat dengan ujian elektrokimia. Lapisan ini telah dikaji pada 3.5% NaCl dan suhu bilik (25 ± 0.2°C). Dalam kajian yang diperolehi, hablur anatase wujud pada suhu 500°C manakala hablur rutil pada 700°C. Nilai kadar kakisan meningkat apabila suhu rawatan haba meningkat dan hasil salutan sol gel terbaik adalah pada 300°C dan kelajuan pengeluaran 60mm/min. Hasil kajian menunjukkan apabila suhu rawatan haba meningkat, kadar kakisan juga meningkat dan ketumpatan kakisan menurun secara beransur-ansur. Selain daripada itu, apabila kelajuan pengeluaran meningkat, zarah filem nipis menjadi lebih padat dan juga saiz bijian menjadi berbeza.
CONTENTS

TITLE i
DECLARATION ii
DEDICATION iii
ACKNOWLEDGEMENT iv
ABSTRACT v
ABSTRAK vi
CONTENTS vii
LIST OF TABLES xii
LIST OF FIGURES xiii
LIST OF SYMBOLS xviii
LIST OF APPENDIX xx

CHAPTER 1 INTRODUCTION 1
1.1 Project background 1
1.2 Problem statement 2
1.3 Objectives 3
1.4 Scopes of study 4
CHAPTER 2  LITERATURE REVIEW  

2.1 Introduction to thin film  
2.1.1 Thin film growth  
2.1.2 Thin film thickness  
2.2 Thin film deposition  
2.2.1 Physical deposition  
2.2.2 Chemical deposition  
2.2.3 Chemical solution deposition / sol-gel  
2.2.3.1 Sol-gel dip coating  
2.2.3.2 Sol-gel densification  
2.3 Introduction to TiO$_2$  
2.3.1 TiO$_2$ crystalline  
2.3.2 Physical and mechanical properties of TiO$_2$  
2.4 Introduction to stainless steel 316L  
2.4.1 Composition of stainless steel 316L  
2.4.2 Physical and mechanical properties of stainless steel 316L  
2.5 Theory of corrosion  
2.5.1 Types of corrosion  
2.5.2 Electrochemical basis of corrosion
2.5.3 Quantitative corrosion theory 39
2.5.4 Polarization resistance 41
2.6 X-Ray diffraction (XRD) 42
2.7 Scanning electron microscopy (SEM) 44
2.8 Fourier Transform Infrared spectroscopy 46

(FTIR)

CHAPTER 3 METHODOLOGY 48

3.1 Introduction 48
3.2 Schematic flow chart of the project 50
3.3 Substrate preparation 51
   3.3.1 Cutting Specimen 51
   3.3.2 Rough Grinding 52
   3.3.3 Polishing 52
   3.3.4 Soldering and painting 53
3.4 Sol gel TiO$_2$ formulation 53
3.5 Sol gel dip coating to produce thin films 54
   of TiO$_2$
3.6 Heat treatment process 56
3.7 Thin film characterization 56
   3.7.1 Fourier transform infrared (FTIR) 57
   3.7.2 X-ray diffraction (XRD) 58
   3.7.3 Scanning Electron Microscopy Observation (SEM) 58
3.8 Corrosion Test
   3.8.1 Corrosion analysis
   3.8.2 IVMAN Software

CHAPTER 4 RESULT AND ANALYSIS

4.1 Introduction

4.2 Structural characterization by X-Ray diffraction
   4.2.1 Effect of calcination temperature to the structural characterization
   4.2.2 Effect of withdrawal speed on the structural characterization

4.3 Structure of molecules by Fourier Transform Infrared (FTIR) spectroscopy
   4.3.1 Effect of withdrawal speed and calcination temperature

4.4 Corrosion rate of stainless steel 316L coating with TiO$_2$
   4.4.1 Effect of calcination temperature to the corrosion rate
   4.4.2 Effect of withdrawal speed to the corrosion rate

4.5 Surface morphology by Scanning Electron Microscopy (SEM)
4.5.1 Effect of calcination temperature to the surface morphology

4.5.2 Effect of withdrawal speed to the surface morphology

CHAPTER 5 CONCLUSION AND RECOMMENDATION 82

5.1 Introduction 82

5.2 Suggestion for future work 84

REFERENCES 85

APPENDICES 92

A Gantt chart Master’s project 1 92

B Gantt chart Master’s project 1 93
LIST OF TABLES

2.1 Mechanical and physical properties of TiO$_2$ 26
2.2 Environmental properties of TiO$_2$ 27
2.3 Composition of stainless steel 316L 28
2.4 Mechanical and physical properties of stainless steel 316L 29
3.1 Weight ratio for TiO$_2$ solution 54
4.1 Comparison of corrosion rate SS 316L coating with TiO$_2$ at different calcined temperature and withdrawal speed 71
4.2 Comparison of MPY with equivalent Metric-Rate expressions 74
4.3 Summarize of relative resistance condition for SS 316L coating with TiO$_2$ at different calcined temperature and withdrawal speed 74
LIST OF FIGURES

2.1 Structure of thin film 5
2.2 Three modes of thin film growth process 7
2.3 Thickness in microns against viscosity in cP for sol-gel thin films 8
2.4 Film thickness against volume percent of TEOS 9
2.5 Thickness against viscosity and speed 10
2.6 Physical vapor deposition process 11
2.7 Sputtering method 12
2.8 Schematic of electroplating process 13
2.9 Spin coating process 14
2.10 Schematic of CVD process 15
2.11 Schematic representation of the sol gel process 16
2.12 Stages of the dip coating process 17
2.13 Schematic of the sol gel preparation of a thin film by dip coating 17
2.14 Schematic drawing of the withdrawal process 18
2.15 Change in fractional thickness as a function of densification temperature 20
2.16 Various types of sintering

2.17 Varieties types of annealing process

2.18 (a) Anatase unit cell, (b) XRD form of TiO$_2$ anatase

2.19 (a) Rutile unit cell, (b) XRD form of TiO$_2$ Rutile

2.20 (a) Brookite unit cell, (b) XRD form of TiO$_2$ Brookite

2.21 A uniform corrosion in an aqueous environment

2.22 Schematic figure of pitting corrosion

2.23 Schematic figure of crevice corrosion

2.24 Photograph of stress corrosion cracking

2.25 Corrosion process showing anodic and cathodic current

Components

2.26 The schematic potentiodynamic polarization behavior of passivating metals

2.27 The schematic of unstable passivation of potentiodynamic polarization

2.28 Classic Tafel Analysis

2.29 XRD patterns of the TiO$_2$ thin films on 316L Stainless steel, calcined at different temperatures of 350-550 °C

2.30 XRD patterns of TiO$_2$ thin film calcined at different temperatures

2.31 SEM Micrographs of TiO$_2$ thin films calcined at various Temperatures

2.32 Infrared spectrum ($\theta=80^\circ$) of sol gel titania film deposited at 30 mm/min and heated up to 400°C
3.1 Flow diagram of full experimental programmed 50
3.2 Diameter of specimen 51
3.3 EDM wirecut machine 51
3.4 Hand grinding machine with 240, 320, 400 and 800 grit 52
3.5 Polisher-grinder machine 52
3.6 Soldering and painting specimen 53
3.7 Solution is mix up and been stirred 54
3.8 Dip coater machine for dip coating process 55
3.9 Drying oven that been used for drying process 55
3.10 Heat treatment process 56
3.11 FTIR principal work and process 57
3.12 XRD working principle and Bragg law 58
3.13 SEM work principal diagram 59
3.14 Connection corrosion cell to potensiostat 60
4.1 XRD patterns at withdrawal speed 6mm/min with different Temperature 63
4.2 XRD patterns at withdrawal speed 30mm/min with different Temperature 65
4.3 XRD patterns at withdrawal speed 60mm/min with different Temperature 65
4.4 Crystallite size of TiO$_2$ films at different temperatures. 66
4.5 XRD patterns at temperature 300$^\circ$C with different withdrawal speed 67
4.6 XRD patterns at temperature 500°C with different withdrawal speed

4.7 XRD patterns at temperature 700°C with different withdrawal Speed

4.8 Crystallite size of TiO$_2$ films at different withdrawal speed

4.9 FT-IR spectra of the SS 316L coated with TiO$_2$ at calcined temperature 300°C and different withdrawal speed (a) 6 mm/min
(b) 30 mm/min, and (c) 60 mm/min

4.10 FT-IR spectra of the SS 316L coated with TiO$_2$ at calcined temperature 500°C and different withdrawal speed (a) 6 mm/min
(b) 30 mm/min, and (c) 60 mm/min

4.11 FT-IR spectra of the SS 316L coated with TiO$_2$ at calcined temperature 700°C and different withdrawal speed (a) 6 mm/min
(b) 30 mm/min, and (c) 60 mm/min

4.12 The microstructure of SS 316L coating with TiO$_2$ heat treated at 300°C (before corrosion): a) withdrawal speed 6 mm/min,
b) 30 mm/min, c) 60 mm/min

4.13 The microstructure of SS 316L coating with TiO$_2$ heat treated at 500°C (before corrosion): a) withdrawal speed 6 mm/min,
b) 30 mm/min, c) 60 mm/min

4.14 The microstructure of SS 316L coating with TiO$_2$ heat treated at 700°C (before corrosion): a) withdrawal speed 6 mm/min,
b) 30 mm/min, c) 60 mm/min
4.15 The microstructure of SS 316L coating with TiO$_2$ heat treated at 300°C (after corrosion): a) withdrawal speed 6 mm/min, b) 30 mm/min, c) 60 mm/min

4.16 The microstructure of SS 316L coating with TiO$_2$ heat treated at 500°C (after corrosion): a) withdrawal speed 6 mm/min, b) 30 mm/min, c) 60 mm/min

4.17 The microstructure of SS 316L coating with TiO$_2$ heat treated at 700°C (after corrosion): a) withdrawal speed 6 mm/min, b) 30 mm/min, c) 60 mm/min
# LIST OF SYMBOLS

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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>Cross-sectional Area</td>
</tr>
<tr>
<td>ASTM</td>
<td>American society for testing and material</td>
</tr>
<tr>
<td>βₐ</td>
<td>Anodic Beta Tafel Constant</td>
</tr>
<tr>
<td>βₖ</td>
<td>Cathodic Beta Tafel Constant</td>
</tr>
<tr>
<td>CR</td>
<td>Corrosion rate</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
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<td>E</td>
<td>Electrode potential</td>
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<tr>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
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<tr>
<td>I</td>
<td>Measured cell current</td>
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<tr>
<td>Iₑₚₑ</td>
<td>Corrosion current</td>
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<tr>
<td>L</td>
<td>Length</td>
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<tr>
<td>M</td>
<td>Number of moles</td>
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<tr>
<td>n</td>
<td>Number of electrons transferred</td>
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<tr>
<td>Symbol</td>
<td>Description</td>
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<td>--------</td>
<td>---------------------</td>
</tr>
<tr>
<td>P</td>
<td>Pressure</td>
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<tr>
<td>Q</td>
<td>Flow Rate</td>
</tr>
<tr>
<td>( R_p )</td>
<td>Polarization resistance</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
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<tr>
<td>T</td>
<td>Temperature</td>
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<td>Velocity</td>
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<td>( \pm )</td>
<td>Tolerance</td>
</tr>
</tbody>
</table>
LIST OF APPENDIX

A  Gantt chart Master’s project 1  95
B  Gantt chart Master’s project 2  96
4.18  Potentiodynamic polarization scan at calcined temperature  94
       300°C and withdrawal speed 6mm/min
4.19  Potentiodynamic polarization scan at calcined temperature  94
       300°C and withdrawal speed 30 mm/min
4.20  Potentiodynamic polarization scan at calcined temperature  95
       300°C and withdrawal speed 60 mm/min
4.21  Potentiodynamic polarization scan at calcined temperature  95
       500°C and withdrawal speed 6 mm/min
4.22  Potentiodynamic polarization scan at calcined temperature  96
       500°C and withdrawal speed 30 mm/min
4.23  Potentiodynamic polarization scan at calcined temperature  96
       500°C and withdrawal speed 60 mm/min
4.24  Potentiodynamic polarization scan at calcined temperature  97
       700°C and withdrawal speed 6 mm/min
4.25  Potentiodynamic polarization scan at calcined temperature  97
700°C and withdrawal speed 30 mm/min

4.26 Potentiodynamic polarization scan at calcined temperature 98

700°C and withdrawal speed 60 mm/min
CHAPTER 1

INTRODUCTION

1.1 Project background

A thin film can be defined as a material that usually had thickness less than 100 μm and been deposited onto a substrate. It is deposited onto the substrate by many processes such as chemical vapor deposition (CVD) or physical vapor deposition (PVD). In case of CVD, the transport of material either takes place through the chemical reaction, while for PVD it applying a current through a target material to knock out the atoms to deposit onto a substrate [1].

Today, thin films are mainly used in order to fulfill more functional purposes. Without most people noticing, thin films are found nearly everywhere around us and related to our daily life; in the automotive industry, as wear-resistant layers in metal-cutting applications, in optical coatings on windows or glasses, in microelectronics, in computer hard disks and not least as decorative films.

The interest on thin films on coating has increased since it is used for cost efficient improvements. Thin films are very essential for protect the materials from atmospheric influences, thermal and also for corrosion protective. There are many applications especially in healthcare industry and household applicants that need used the role of surfaces of substrates because of its cleanliness. Recently, many
researchers have developed various methods to apply Titanium Dioxides (TiO$_2$) coating on various substrates [2].

Supported TiO$_2$ thin films can be obtained by different thin film processing techniques including sputtering, chemical vapour deposition [3], e-beam evaporation and sol gel process [4]. Among these processes, sol gel offer potential advantages and is a versatile technique for metal oxides preparation [5]. The main advantages of this technique are low cost, a low temperature process, a controlled level of porosity, the ease of doping and composite preparation, no need for machining and also high homogeneity. The use of sol gel process for pretreatment of metallic surfaces is a relatively new approach in surface engineering and corrosion protection. It is one of the efforts to replace traditional, environmentally hazardous and more expensive materials.

The aim of this work is to deposit TiO$_2$ coating on 316L stainless steel with the effect of withdrawal speed and heat treatment. In this study, the TiO$_2$ thin film is investigated at different calcinations temperatures in order to obtain different sizes of crystallites which may leads to the higher porosity surface of the thin film. The results of mechanical tests were interpreted by means of microstructural analysis (SEM), crystalline phase determination (X-Ray diffraction) and Fourier Transform Infrared Spectroscopy (FTIR). Other than that, the corrosion rate of it was interpreted through electrochemical test since TiO$_2$ are widely used in the form of coatings as corrosion protection and wear resistant materials.

1.2 Problem statement

Currently, stainless steel is widely used in many applications such as furnace parts, heat exchangers, and tubing that related to heat and also for marine application. There are a highly demands for stronger, more corrosion resistant and lighter materials as well as reproducible methods for producing such materials.
But, fouling deposition and localized corrosion on the heat-transfer surfaces or marine application of the stainless steel equipment often simultaneously exist, which can introduce additional thermal resistance to heat-transfer and damage equipment surfaces. It is a good anticorrosion way to coat a barrier layer of certain materials on the metal surface such as by coated using TiO$_2$.

A protective coating deposited to act as a barrier between the surfaces of the component and the aggressive environment that it is exposed during operation is now globally acknowledged to be an attractive means to significantly reduce damage to the actual component by acting as the first line of defense. Coating is a layer of material formed naturally or synthetically or deposited artificially on the surface of an object made of another material with the aim of obtaining required technical properties.

Type 316L stainless steel was chosen taking into account the heat treatment necessary for the densification of the coatings. Therefore, low carbon content steel was judged more convenient since it is less susceptible to sensitization which might promote an enhanced corrosion. In addition, 316L stainless steel is a material widely used in chemical industry environments.

1.3 Objectives

i. Deposited of TiO$_2$ coating on 316L stainless steel with the effect of withdrawal speed and calcination temperature.

ii. Effect of withdrawal speed and calcination temperature on surface characterization and corrosion behavior of the TiO$_2$ coating.
1.4 **Scopes of study**

i. Sol preparation of TiO$_2$ by Titanium (IV) butoxide (TBOT), ethyl acetoacetate (EAcAc) and Ethanol (EtOH) with molar ratio of 1:1:20.

ii. TiO$_2$ coating was deposited by dip coating process on stainless steel 316L.

iii. Different withdrawing speed (6mm/min, 30mm/min, 60mm/min).

iv. Different calcination temperature (300°C, 500°C and 700°C).

v. Characterizations by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscope (SEM), and electrochemical test.

1.5 **Significance of study**

The significance of this study is to ensure that TiO$_2$ sol-gel coating was able to be deposited onto 316L stainless steel substrate by using TiO$_2$ formulation with a method by sol-gel dip coating deposition. Thus, this material will be applied to all related industry for better enhancement of future prevented fouling deposition and corrosion surface.
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to thin film

A thin film is defined as a low dimensional material created by condensing, atomic/molecular/ionic and one by one species of matter. It also can be defined as a material that normally less than 100 μm in thickness. It is a branch that deals with thin layers of different materials. Thin films are fabricated by deposition individual atoms on a substrate. Figure 2.1 show the dimensional structure of thin films.

Figure 2.1: Structure of thin film [6]
Thin films, interfaces and surface layers had a crucial role in many industries that used modern technology such as solar cells, electronic semiconductor devices, batteries, nano technology and optical coatings [6]. For improving their functionality, the atomic structures of selected materials are importance. Historically, thin films have been used for more than half century in making decorative parts, optical coating, electronic devices and instrument hard coatings. Other than that, thin films are essential for protect materials from others influences such as from atmospheric and thermal [7].

As a two dimensional system, thin films are important to many real world problems. Thin films compared to other, it had low cost on materials than corresponding bulk material. It also can perform the same function when it comes to surface processes.

2.1.1 Thin Film Growth

Normally, thin film does not growth as perfect slabs of bulk materials. Physical properties of thin films on substrate are different when compared to bulk material especially things on structure and development of morphology. Deposition conditions can influence a feature like orientation, size, shape and other at an early stage of nucleation and growth [8]. The growth process include a statistical process of nucleation, surface diffusion controlled growth of the three dimensional nuclei and formation of a network structure and its subsequent filling to give a continuous film. There are three modes of thin film growth process which are island type (Volmer-Weber type), layer type (Frank-van der Merwe type) and mixed type (Stranski-Krastanov type) [9].
2.1.2 Thin film thickness

The film is under a tensile stress after gelation process since it bonds to the substrate surface and shrinks as it dries. This will result cracking in the film. However, it can be avoided if the film is less than a certain critical thickness. The thickness of the film is resulted depends on different variables that can be controlled. If the film is too thick, the film will be shrinking in the direction parallel to the substrate surface cause of the coherent force within the film. This occurs when it is heated to drive out the remaining water and solvent. Cracking will be happened if the coherent force is too large. Meanwhile for thinner film, it will strongly attach to surface as the bonding force prevents the shrinkage in the direction parallel to the surface. The ideal thickness, obtained by one coating, should be between 0.1 and 0.45 μm [10].

Final film thickness is depending on several factors such as viscosity, H₂O/TEOS (tetraethoxysilane) ratio, and the withdrawal speed. In order to get the ideal thickness of the film, these factors can be controlled to ensure it produce dense and smooth film.
2.1.2.1 Effect of viscosity

Viscosity of the coating solution can affect the final film thickness as more viscous the solution, more of it will “stick” to the substrate surface producing a thicker film. Based on Figure 2.3 below, the final thickness is increases as the viscosity increases that resulting films with too many cracks.

![Viscosity vs Thickness Graph](image)

Figure 2.3: Thickness in microns against viscosity in cP for sol-gel thin films [11]

2.1.2.2 Effect of density

The density of the final film also could be affected by H$_2$O/TEOS ratio. Figure 2.4 shows that H$_2$O/TEOS ratio increases as the initial density of the films increases because during heated at high temperature, it did not compact. Therefore, by adding more TEOS and reducing the H$_2$O/TEOS ratio will result in thicker films. This plot also shows that by adding ethanol at constant H$_2$O/TEOS ratio will produced thinner films.
2.1.2.3 Effect of withdrawal speed

The withdrawal speed as the slide is lifted from the sol-gel solution also affects the thickness of coating. There are six different forces that govern the final thickness of the film during the film deposition: (1) viscous drag upward on the liquid by the moving substrate, (2) force of gravity, (3) resultant force of surface tension in the concavely curved meniscus, (4) inertial force of the boundary layer liquid arriving at the deposition, (5) surface tension gradient, and (6) the disjoining or conjoining pressure (important for films less than 1μm thick) [13].

\[
h = c_1 \sqrt{ \frac{\eta U}{\rho g}}
\]  

(2.1)

Where \( h \) is the thickness, \( c_1 \) is the proportionally constant (about 0.8 for Newtonian liquids), \( U \) is the withdrawal speed, \( \eta \) is the viscosity, \( \rho \) is the density and \( g \) is the acceleration due to gravity [10].

Figure 2.4: Film thickness against volume percent of TEOS [12]
Based on previous study by Strawbridge and James, the increasing value of the withdrawal rate will increase the thickness of the coating [14]. Based on Figure 2.5, at the velocity that will be used in this study, 3 cm/min, the coatings will be in range from 0.2 to 0.6 μm. This is crucial since this range of thickness will result in mostly crack free coatings. According to Shen, et al. [15], TiO₂ particle coating with about 460 nm thickness exhibits the best corrosion resistance because of its perfect structure in the coating. However, thicker or multiple coating will resulting in worse corrosion resistance because the films subjected to residual tension experience both upward and lateral deflections, thus inferring mixed conditions.

### 2.2 Thin film deposition

Thin film deposition is defined as the act of applying or any technique for depositing thin film onto a substrate surface or previously deposited layer. A solid material is considered to be in thin film form when it is grown as a thin layer on a substrate by controlled condensation of molecular, individual atomic or ionic species by ultra-
chemical reactions or physical process [16]. There are many deposition techniques for material formation and basic techniques are either purely physical or purely chemical [17].

2.2.1 Physical deposition

Physical deposition method uses thermodynamic, mechanical or electromechanical to produce a thin film of solid. This method required low vapor environment to function properly and most of it can be classified as physical vapor deposition (PVD) [18].

![Physical vapor deposition process](image)

**Figure 2.6: Physical vapor deposition process [18]**

PVD is the method used to deposit thin layers of material by condensation of vapor in a vacuum environment and high temperature. Based on Figure 2.6, the substrate is placed in entropic and energetic environment to ensure that the particles of material leaving its surface. In order to form a solid layer, a cooler surface which draws energy from these particles is placed facing the source. The particles are allowed to travel freely when it is kept in a vacuum deposition chamber. Films deposited by physical are commonly directional since the particles tend to follow a straight path. One of the examples of physical deposition is sputtering.
2.2.1.1 Sputtering

This method relies more on plasma like a noble gas such as argon to hit material from a target a few atoms at a time. It is one of the most flexible deposition techniques since the target can be kept at a relatively low temperature. Sputtering is more useful for mixture or compounds where it tend to evaporate at different rates. Sputtering is widely used in manufacturing of CD, BD and DVD [19]. Step’s coverage is almost conformal. This method provides a good thickness control and also a fast technique.

![DC plasma sputtering](image)

Figure 2.7: Sputtering method [19]

2.2.2 Chemical deposition

In this method, a fluid precursor wills leaving a layer after it undergoes a chemical change at a solid surface. It can be found in our daily life as it is place in the flame for formation of soot on a cool object. Deposition happens on each surface since the fluid are surrounds the solid object. Thin films that been produced from chemical deposition techniques tend to be conformal rather than directional. This method can be further categorized by the phase of the precursor:
2.2.2.1 Plating

This method relies on liquid precursors such as a solution of water with salt of the metal to be deposited. The most commercially process is electroplating. In this process, the target object or sample is immersed in a chemical bath that contains dissolved metal atoms such as gold. Atoms will be deposited onto the sample as an electric current been applied between the sample and chemical bath [20]. Figure 2.8 below show the schematic of electroplating process. This method has been widely used to make chrome automobile bumpers, plated silverware and many other applications.

![Figure 2.8: Schematic of electroplating process [20]](image)

2.2.2.2 Spin coating

In this technique, a solution that normally contains a polymer and a solvent has been applied to the center of flat substrate. Then, the spin coater with a high speed will rotate the substrate in order to spread the fluid by the centrifugal force. A thin layer
of polymer will be left on the substrate since the solvent is volatile. Figure 2.9 below show the spin coating process. The thickness of the film are depends on the speed and the viscosity of the sel. In order to increase the thickness of the films, repeated depositions can be applied. Other than that, thermal treatment is normally been carried out to crystallize the amorphous spin coated film. Such crystalline films can exhibit certain preferred orientations after crystallization on single crystal substrate [21].

![Spin coating process](image)

Figure 2.9: Spin coating process [21]

### 2.2.2.3 Chemical vapor deposition

Chemical vapor deposition is a chemical process used to produce high performance and high purity solid materials. It is normally used in the semiconductor industry to produce thin films. The chemical vapor deposition involves a flowing of precursor gases into a chamber that containing heated objects to be coated. Deposition of a thin film on the surface exists when chemical reactions occur near the hot surfaces. Then, the productions of chemical by products are exhausted out of the chamber together with unreacted precursor gases [22].
2.2.3 Chemical solution deposition or sol-gel method

This process uses a liquid precursor that normally used like organometallic powders dissolved in an organic solvent. It is also relatively inexpensive and easy to process. Simple thin film that been produced can produce stoichiometrically accurate crystalline phases. This technique also known as the sol-gel method because of the ‘sol’ or solution been gradually evolves towards the formation of a gel.

Sol gel technique has more advantages rather than other processing technique. It is applicable for complex substrate geometries by particle such as dip coating since it is a low temperature aqueous technique. In addition, its chemistry can be controlled in order to change the microstructure, surface area also size and scale of porosity.

In the previous study investigated by Page, et al. [23], the solution of TiO$_2$ was formulated through a combination of chemicals. The crystalline products can be produced either by having TiO$_2$ in terms of thin film or powder. Figure 2.11 shows the schematic of sol gel process which in order for the sol to become powder; it was transformed in different process. The sol was configured from the addition of precursor, catalyst and solvent which that left to become gel. Then, gel that been
produced been drying in room temperature or at most 70°C for 24 hours to ensure that water or alcohol trapped in matrix will be remove [24]. It was followed by calcination process of xerogel at high temperature which typically in range 450°C to 500°C that resulting in crystalline TiO₂.

Figure 2.11: Schematic representation of the sol gel process [23]

2.2.3.1 Sol-gel dip coating

Sol gel process in Figure 2.11 above resulted in solid powder and not in a thin film. Dip coating method is the thin film strategy in process of modified sol-gel onto a form of thin film. Dip coating is a process of immersing a substrate into a tank containing coating material, then removing the piece or substrate from the tank and allowing it to drain [25]. The substrate or coated piece can be dried either by baking or force-drying.

Basically, dip coating process can be separated into three stages as can be seen in figure 2.12 below. First stage is immersion which substrate is immersed into the solution of coating material at a constant speed. Second stage is dwell time where the substrate is remains fully immersed and static that allows the coating material to apply itself onto the substrate. Third stage is withdrawal which the substrate is
withdrawn at a constant speed. The faster withdrawn speed will result in the thicker the coating material that will be applied to the substrate.

Figure 2.12: Stages of the dip coating process [25]

Figure 2.13 shows the sol gel preparation of a thin film by dip coating. The substrate were dip coated with the liquid sol-gel solution which resulting a thin layer of sol-gel on the surface. The dipping process is very important to the properties of the final thin film.

Figure 2.13: Schematic of the sol gel preparation of a thin film by dip coating [23]

Generally, stabilization condition of sole particles is follows the stern’s potential consideration [26]. According to stern’s theory, the gelation process is
approaching of the charge particle to distances below the repulsion potential. After that, the gelation process is changed to an attraction leading to a very fast gelation. This process takes place at the gelation point as show in Figure 2.14. Then, the resulting gel has to be densified by thermal treatment and the densification temperature is depending on the composition.

Figure 2.14 shows the steady-state deposition stage of the dip coating process [27]. As can be seen, the dilute sol is drawn upwards gravitational draining. Then, it went through an evaporation process of both water and ethanol that combine to shrink the film into a gel. A dense sol gel thin film remains once it has fully collapsed.

![Schematic drawing of the withdrawal process](image)

Figure 2.14: Schematic drawing of the withdrawal process [28]

The advantages of casting as a thin film is it can quicken the drying of precursor. Thin film precursor is formed on the substrate immediately with minimal drying. The coated substrates are then calcined at temperature 500°C to produce crystalline and dense thin films. Dip coating process are widely used for solar energy control systems and anti-reflective coatings on windows. It is also applied for
optical coatings like on bulbs, optical filters for dielectric mirrors and fabricating multilayer systems [29].

2.2.3.2 Sol-gel densification

After coated, the densification process will be done by heating the sol-gel thin film to high temperature in order to make a smoother and compact surface. While gel had been shrinking, the gel network will continuously deform and the remaining liquids are out of the film through pores causes strains and stresses shrinking gel. The gel must be heated to high temperatures in order to make it pore-free, as smooth and as dense as possible.

Once it had been coated, the slides are heated in an oven with the desired densification temperature and at a constant rate of approximately 120°C/hour. This constant rate will help to prevent cracks from forming in the film. Based on the study by Klein et al [30], this rate is the best to allow both of gel microstructure to collapse due to allow the gases to escape and to reduce viscosity. It was important to ensure that the heating rate not exceeds 120°C/hour or the film will slightly crack. Slides are left for one hour after it reached the desired temperature. After that, oven is turned off and let the slides to cool down or reduced to room temperature overnight inside the oven.

Based on previous study investigated by Hsu et al. [31], the final densification temperature was determined according to data shown in Figure 2.15 below. This figure shows the fractional change in coating thickness of sol-gel films in respect to temperature. It can be seen that the film has become fully densified at temperature above 500°C as the thickness of the film does not significantly changed. Therefore, the densification temperature that will be used to densify the coatings is 500°C.
There are varieties of heat treatment process available for sol gel densification. Some of it are sintering, annealing and calcination.

2.2.3.2.1 Sintering

Sintering can be defined as a processing technique used to produce density-controlled materials and components from metal or ceramic powders by applying thermal energy. Sintering is the method involving consolidation of powder grains by heating the “green body” to a high temperature below the melting point, when the material of the separate particles diffuse to the neighbouring powder particles.

It can be categorized to several categories as shown in Figure 2.16 below. Solid state sintering is occurs when the powder compact is densified wholly in a solid state at sintering temperature while liquid phase sintering occurs when a liquid phase is present in the powder compact during sintering [32]. Other types of sintering are vapour phase sintering, transient liquid phase sintering and viscous flow sintering.
The purpose of sintering is to produce sintered parts with reproducible and if possible designed microstructure through control of sintering variables. This process consolidates the material, increases its strength and usually causes it to shrink.

![Figure 2.16: Various types of sintering [32]](image)

2.2.3.2.2 Annealing

Annealing is the process of softening steel by a heating and cooling cycle to ensure it can be bent or cut easily. In this process, steel will be heated above the transformation temperature to form austenite and cooled very slowly. There are varieties types of annealing such as blue annealing, black annealing, intermediate annealing, bright annealing, soft annealing, finish annealing and recrystallization annealing. They are applied according to the product properties in the industry.

Annealing process is commonly applied in the sheet and wire industries. The temperatures that normally been used from 550°C to 650°C. In full annealing, cooling must be unsure to take place very slowly to allow coarse pearlite formed. There are three stages of annealing process. First stage is recovery which occurs at
the lower temperature stage and before the appearance of new grains [33]. Second stage is recrystallization where new grains nucleate and grow in order to replace the deformed by internal stresses [33]. Third stage is grain growth which the microstructure starts to coarsen and may cause metal to lose substantial parts of its original strength.

Figure 2.17: Varieties types of annealing process [33]

2.2.3.2.3 Calcination

Calcination is a thermal treatment process applied to ores and other solid materials in order to bring out a thermal decomposition, phase transition or removal of a volatile fraction [34]. It is the process of subjecting a substance to the action of heat that resulting in change in its physical or chemical constitution. Normally, the purpose of calcination is to drive of water that present as absorbed moisture. Other than that, it drives off carbon dioxide or other volatile constituent. This process is also to oxidize a part or the whole of the substance.

The calcination process normally takes place at temperatures below the melting point of material. Calcination is carried out in furnaces or reactors of various
designs including rotary kilns, fluidized bed reactors, multiple health furnaces and shaft furnaces.

2.3 Introduction to TiO$_2$

TiO$_2$ is the naturally occurring oxide of titanium with chemical formula TiO$_2$. It also known as titanium oxide or titania. According to the United Nations’ (UN) Globally Harmonized System of Classification and Labeling of Chemicals (GHS), TiO$_2$ is a white solid organic substance which non-flammable, not classified as hazardous, thermally stable and poorly soluble [35]. TiO$_2$ is a semiconductor material that been used in a wide variety of applications. TiO$_2$ is well known as environment purification, an effective photocatalyst for water, self-cleaning surfaces and also bactericidal material (strong oxidation activity and superhydrophilic property) [35, 36]. TiO$_2$ found in nature in variably coloured due to the presence of impurities or other elements. In order to produce pure TiO$_2$, processing is necessary. Large crystals of pure TiO$_2$ are transparent.

2.3.1 TiO$_2$ crystalline

Crystalline TiO$_2$ exists in three phases; anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic) [37]. Each crystalline phase highly depends on sol composition, calcinations and temperature. During calcination, TiO$_2$ film can be transforming from amorphous phase into crystalline anatase and followed by rutile phase.
2.3.1.1 Anatase

Anatase is always found as sharply, small and isolated developed crystals that been crystallizes in the tetragonal system. Anatase shares some mostly same properties as rutile such as density, hardness and luster. Crystal of anatase is not easily confused with any other mineral since they are very distinctive. The anatase form of TiO$_2$ consists of distorted TiO$_6$ octahedrons where two oxygens closer to titanium centre than the other four [38]. Eight faced tetragonal dipyramids that come to sharp elongated points is form. Each octahedron will be share four edges with others. There are six oxygen that near to titanium and three titanium that nearest to oxygen. Figure 2.18 (a) shows anatase unit cell.

![Anatase unit cell](image)

Figure 2.18: (a) Anatase unit cell, (b) XRD form of TiO$_2$ anatase [38]

Anatase is kinetically stabilized since it is not an equilibrium phase of TiO$_2$. It will be transforms to equilibrium rutile phase at temperature ranges from 550$^\circ$C to 1000$^\circ$C. However, the temperature of this transformation is depends on the impurities present in the material and morphology of the sample [39].
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