SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

KINETIC MODELLING OF THE FORMATION OF TITANIUM HYDRIDE FROM THE REACTION BETWEEN MAGNESIUM HYDRIDE AND TITANIUM TETRACHLORIDE USING MATLAB

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Kinetic Modelling of the Formation of Titanium Hydride From the Reaction Between Magnesium Hydride (MgH_2) and Titanium Tetrachloride ($TiCl_4$) using Matlab**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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LIST OF SYMBOLS

A	Reactant gas
B	Product gas
C_p	Specific heat capacity
D_{AB}	Binary diffusivity of gas A and B
e	Thermal emissivity
E_a	Activation energy
G	Gas flow rate
H	Standard Entalphy of reaction
k	Thermal conductivity
k_p	Thermal conductivity of porous product
K_{eq}	Equilibrium constant
M1	Molecular Weight of Species 1
M2	Molecular Weight of Species 2
n_A	Molar rate of species A
n_B	Molar rate of species B
n_C	Molar rate of species C
Nu	Nusselt Number
P_A	Partial pressure A
P_B	Partial pressure B
P_r	Partial pressure C
R	Correlation Factor

R’	Fractional Reaction
R	Gas constant
r_i	Inner radius of Shell i
R_{WP}	Weighed profile factor
ρ	Density
ρA	Density of Species A
ρB	Density of Species B
ρc	Density of Species C
r	Collision Diameter
Re	Reynold number
Ro	Radius of pallet
Sc	Schmidht number
Sh	Sherwood number
Tc	Core temperature
Tg	Gas temperature
Tp	Product temperature
Ts	Surface temperature
θ	Porosity
Xh	Degree of hydriding
Xw	Weight different
W_f	Final weight
W_i	Initial weight

LIST OF ABBREVIATION

ANOVA	Analysis of Variance
BEPM	Blended Elemental Powder Metallurgy
CMP	Chemical Mechanical polishing
DOE	Design of Experiment
EDX	Energy Dispersive X-ray
ETC	Edge to centre
FT-IR	Fourier Transform Infra Red
H_2	Hydrogen gas
ICSD	Inorganic Crystal Structure Database
$MgCl_2$	Magnesium Chloride
MgH_2	Magnesium Hydride
NaOH	Sodium Hydroxide
SCM	Shrinking Core Model
SEM	Scanning Electrn Microscopy
TGA	Thermogravimetric analysis
Ti	Titanium
$TiCl_4$	Titanium Tetrachloride
TiH_2	Titanium Hydride
$TiO2$	Titanium dioxide

PEMODELAN KINETIC BAGI PEMBENTUKAN TITANIUM HIDRIDA DARI REAKSI ANTARA MAGNESIUM HIDRIDA DAN TITANIUM TETRAKLORIDA MENGGUNAKAN MATLAB

ABSTRAKS

Tindak balas antara magnesium hidrida (MgH_2) dan titanium tetraklorida ($TiCl_4$) untuk menghasilkan titanium hidrida (TiH_2) telah dijalankan dengan mengubah beberapa parameter seperti suhu tindakbalas, masa tindakbalas dan kadar aliran gas argon. Eksperimen ini dilakukan dengan menggunakan Designs Expert 8 (DOE). Suhu pengklorinan telah diubah dari 200°C hingga 300°C, manakala masa tindakbalas telah diubah dari 60 minit hingga 180 minit. Kadar aliran gas argon dikawal 20-60 $cc.min^{-1}$. Pencirian bahan mentah telah dilakukan dengan menggunakan pembelauan sinar-X (XRD), mikroskop elektron pengimbas (SEM), dan serakan tenaga X-ray (EDX), analisis termogravimetri (TGA), dan elemental (CHNS). Dari eksperimen yang telah dijalankan, perbezaan nilai berat yang paling besar (XW) ialah 0.19% dan tahap hidriding (XH) 38.49% telah berlaku pada keadaan 300°C selama 180 minit dengan 20 $cc.min^{-1}$ kadar aliran gas argon. Keputusan DOE telah menunjukkan bahawa masa tindakbalas telah dikenalpasti sebagai faktor yang paling penting diikuti oleh kadar aliran gas argon dan suhu tindak balas. Analisis fasa menunjukkan baki sampel terdiri daripada MgH_2, $MgCl_2$, $TiCl_{2.3}$ dan TiH_2. Fasa kecil seperti TiO_2 juga kelihatan yang menunjukkan beberapa kebocoran berlaku semasa tindak balas. Dari hasil simulasi, isotherma dan bukan isotherma model teras mengecut (SCM) telah digunakan untuk mengkaji tindak balas. Isotherma SCM menunjukkan keputusan yang paling hampir dengan data eksperimen berbanding dengan bukan isotherma SCM.

KINETIC MODELLING OF THE FORMATION OF TITANIUM HYDRIDE FROM THE REACTION BETWEEN MAGNESIUM HYDRIDE AND TITANIUM TETRACHLORIDE USING MATLAB

ABSTRACT

The reaction between Magnesium Hydride (MgH_2) and Titanium Tetrachloride ($TiCl_4$) to produce Titanium Hydride (TiH_2) were carried out by varying the reaction temperature, reaction time and argon gas flow rate. The experiment was performed by statistical design of experiment (DOE). The chlorination temperature was varied from 200 - 300°C, while the reaction time was changed from 60 - 180 minutes. The argon gas flow rate was controlled from 20 to 60 $cc.min^{-1}$. Samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray (EDX), Thermogravimetric analysis (TGA), and Elemental (CHNS). From the experiments, the highest weight different (Xw) of 0.19% and degree of hydriding (Xh) of 38.49% was measured at 300°C for 180 minutes with 20 $cc.min^{-1}$ of argon gas flow rate. The DOE analysis was performed and reaction time was determined as the most significant factor followed by flow rate of argon gas and reaction temperature. Phase analysis indicated the residual samples composed of MgH_2, $MgCl_2$, $TiCl_{2.3}$ and TiH_2. Minor phases such as TiO_2 was observed which indicated some leakage occur during the reaction. From the simulation results, the isothermal and non-isothermal Shrinking Core Model (SCM) were used to study the reaction. From the results, Isothermal shrinking core model shows nearest approximation to the experimental results compared to non-isothermal shrinking core model.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Titanium (Ti) has excellent properties such as low density, high strength, and also high corrosion resistance. Besides that, its mineral resources are abundant and it has potential to be a common structural material for the next generation (Oi, Okabe, et al.(2004)). However, the cost of the production of the titanium is very high. Titanium is commercially produced by the magnesiothermic reduction of titanium tetrachloride ($TiCl_4$) which is also known as Kroll process. In Kroll process, the temperature for metal magnesium to reduce titanium tetrachloride ($TiCl_4$) in an airtight metallic reactor is about 1100 K (Figure 1). The titanium deposit will stick to the wall of the reactor and keep growing grows in the form of massive sponge. As a result, it is rather difficult to recover product titanium (Okabe, et al. 2004).

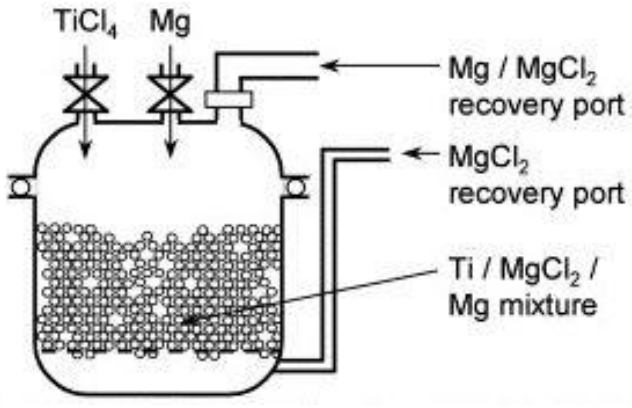


Figure 1: Kroll process (Okabe, 2004).

In order to overcome the high-cost problem in the production of titanium, blended elemental powder metallurgy (BEPM) method is used (Duz et al., 2016). This method uses the low cost starting blends of titanium powder and alloying powders. This method potentially the lowest cost manufacturing process in order to attain desirable properties of produced titanium alloys. The relative densities of the produced titanium alloys must be greater than 98% of the theoretical densities. However, the relative densities of the titanium alloys produced by BEPM do not exceed 95% (Duz et al., 2016). In order to increase the relative densities of the titanium alloys produced, titanium hydride (TiH_2) is used as the starting material instead of conventional titanium powder. Therefore, this project is about to form the titanium hydride (TiH_2) from the reaction between magnesium hydride (MgH_2) and titanium tetrachloride ($TiCl_4$).

Magnesium hydride (MgH_2) is a material of the most interest for a number of technical applications, mainly as hydrogen storage material for proton exchange membrane (PEM) fuel cells as it has large reversible storage capacity (7.6 mass%) of high purity hydrogen. In addition, the value of enthalpy for hydride formation is a large number which is, ΔH=−75 kJ/mole thus making magnesium also attractive for thermal energy storage. These features, combined with the low cost of magnesium, provide an excellent potential for hydrogen-related applications (Zaluska et al., 1999). Magnesium also has a relatively high abundance in earth (Perejón et al., 2016). However, the kinetic absorption and also desorption of hydrogen is slow and this will make the actual application of magnesium hydride is limited (Huot et al., 1999). Thus, magnesium hydride needs higher temperature compared to other metal hydride system (Kyoi et al., 2004). The temperature must be above 673K (Kyoi et al.,

2004). Magnesium hydride (MgH_2) is considered as one of hydrogen storage materials (Klimkowicz et al., 2015).

Titanium tetrachloride ($TiCl_4$) is a colourless to pale yellow liquid with a strong penetrating odour that is the most toxic of the titanium compounds (Kapp et al., 2014). Some of other properties of titanium tetrachloride are highly corrosive, acute irritant to the skin, eyes, mucous membranes, and the respiratory tract that can be lethal or can cause permanent injury due to acute or chronic exposures encountered in normal use. The expected chemical reaction between magnesium hydride and titanium tetrachloride is as following:

$$2MgH_2 + TiCl_{4(g)} = TiH_2 + 2MgCl_2 + H_2(g),\ \Delta G°(kJ/mole) = -0.0393*T - 488.42 \quad (1.1)$$

On the other hand, in order to perform kinetic modeling for the gas-solid reaction, MATLAB was used for the simulations. Models that are used to predict the reaction between the magnesium hydride and $TiCl_4$ is known as Shrinking Core Model and Cracking Core Model.

1.2 Problem Statement / Project Significant

Research of kinetic reaction between magnesium hydride and titanium tetrachloride to produce titanium hydride is less. This kinetic modelling can shows how fast the reaction happen. Furthermore, the production of titanium powder is a highly cost production. As example in Kroll process, the temperature for metal magnesium to reduce titanium tetrachloride ($TiCl_4$) in an airtight metallic reactor is about 1100 K. Titanium alloy that was produced by conventional titanium powder as starting material has low relative densities. To produce titanium alloys that have high relative densities, titanium hydride powder must be used as a starting material.

1.3 Objective

There are some objective that have been set and to be accomplished:

1. To develop kinetic modelling for the formation of titanium hydride from the reaction between titanium tetrachloride ($TiCl_4$) and magnesium hydride (MgH_2) in different parameters: furnace temperature, reaction time, and flow rate of the career gas by using MATLAB software.
2. To produce titanium hydride by using low temperature process and low cost.
3. To define the best results between isothermal and non-isothermal model with experimental results to access the accuracy of the model developed.

1.4 Scope of Project

There are three parts in this project which are experimental work, statistical analysis and kinetics simulations. For the first part which is experimental work, the raw MgH_2 powder was being analysed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) for characterization on the surface morphology and also the purity of the sample. Then the sample was reacted with $TiCl_4$ in a quartz tube and the percentage of the weight different, Xw(%) was determined. After the reaction was done, the residual samples was analysed by XRD, SEM/EDX. Any changes in the morphology as well as phases was recorded.

For statistical analysis part, Design Expert v8.0.6 software was used in order to construct the matrix of Design of Experiment (DOE). Analysis was done on the data retrieved and it was crucial to gain deeper understanding and insight to the reaction. For the final part of this project which is kinetic simulations, kinetic modelling was performed using MATLAB R2014a software. The models used for this kinetic modelling are Shrinking Core

Model (SCM). The predicted reaction rate and experimentally determined reaction rate for the reaction was compared and analysed.

1.5 Outline

In this thesis, Chapter 1 give some explanations about the overview of the project. This will include the objective of this project, problem statement, and also the scope of the project. For Chapter 2, it will review about the researches that have been done. Chapter 3 will explain more about the experiment methodology that had been used. Chapter 4 will discuss more about the kinetic simulation and also the calculation of the various constant. All the experimental results as well as the results from the kinetic simulation will be discuss and analysed in Chapter 5. Conclusion and recommendation are in Chapter 6 and lastly all the reference will be put in Chapter 7.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Titanium was acknowledged for its strategic importance as it has very unique properties such as lightweight, high strength alloyed, structurally efficient metal for critical, high-performance aircraft, such as jet engine and airframe components (Donachie et al., 2000). Today, titanium and its alloys are extensively used for aerospace, industrial and consumer applications. Titanium is also being used in the following applications such as spacecraft, chemical and petrochemical production, hydrocarbon production and processing, automotive components, food and pharmaceutical processing, recreation and sports equipment, medical implants and surgical devices (Donachie et al., 2000). Titanium alloys are considered to be the most attractive metallic materials for biomedical applications (Elias et al., 2008). Since the properties of titanium are very attractive, market demand become huge day by day.

However, the main problem in the production of titanium is the cost which is very high. Blended elemental powder metallurgy (BEPM) method has been developed in order to overcome this problem. This method required titanium hydride as a starting material as titanium hydride can help to increase the relative densities of the titanium alloys produced. Hence, in this project, the reaction between magnesium hydride (MgH_2) and titanium tetrachloride ($TiCl_4$) has been done as one of the way to produce titanium hydride powder.

Metal hydrides compose of metal atoms that constitute a host lattice and hydrogen atoms. There are two different types of hydrides which are α-phase and β-phase. α-phase is defined when there is only some hydrogen that have been absorbed while β-phase is when

hydride is fully formed. Types of metals differ in the ability to dissociate hydrogen as the ability is depend on surface structure, morphology and purity (Sakintuna et al., 2007). Examples of the metal hydrides are nickle hydride (Feng et al., 2001), vanadium hydride (Kyoi et al. 2004), boron hydride (Muetterties et al., 2012), sodium aluminium hydride (Bogdanović et al. 2000), lithium aluminium hydride (Hydride et al., 1986), calcium hydride (Cech et al., 1974).

2.2 Design Of Experiment (DOE)

Design of experiment (DOE) is used to assess the input factors and interactions that are important to our response (Khan et al.,2013). The important factors and interactions are identified also can be identified using DOE. There are three types of DOE which are namely screening DOE, characterization DOE, response surface design and Taguchi design. Design of experiment or more commonly abbreviated as DOE, is a very powerful tool for the industry to study about the interactions between factors and isolating factors and determining the most influential one (Antony, 2003).

In the research done by (Viviani et al., 2000), the effect of a selected number of parameters of the Low-Temperature Aqueous Synthesis (LTAS) on $BaTiO_3$ particle size was investigated by the statistical design of experiment approach. The parameters that have been used are solution concentration, stirring energy and precursors mixing condition. ANOVA method was used for the statistical analysis of experimental results. The significance of such parameters, together with the apparent ineffectiveness of the ageing time, was discussed (Viviani et al., 2000).

In another research which also used design of experiment are had been done by (Kim et al., 2006). For this research, design of experiment (DOE) was performed to investigate the interaction effect between the various parameters as well as the main effect of each parameter during copper chemical mechanical polishing (CMP). Statistical analysis techniques are used to get a better understanding of the interaction behaviour between the various parameters and the effect on removal rate, non-uniformity and ETC (edge to centre). For experimental tests, the optimized parameters combination for copper CMP which were derived from the statistical analysis could be found for higher removal rate and lower non-uniformity through the above DOE results (Kim et al., 2006).

Both of the mentioned above are the examples of the experiments that used DOE approach in order to generate the design scheme of the study. In this research, similar approach was employed too. For each parameter, 2 levels were set, which were high (1) and low (-1). Centre points were added to act as the control point for the experiment. In this research, 3 control points were added.

2.3 Formation of Titanium Hydride

In this chapter, the reaction process to form titanium hydride was highlighted. Magnesium hydride will be reacted with titanium tetrachloride in order to form titanium hydride. Magnesium hydride and titanium tetrachloride are two main compound in this research. The method to characterize the sample was reviewed too.

2.3.1 Magnesium Hydride

Magnesium hydride is a material of the most interest for a number of technical applications, mainly as hydrogen storage material, due to its large reversible storage capacity (7.6 mass%) of high purity hydrogen (Perejón et al., 2016). Magnesium hydride also can be used as a thermal energy storage system in thermosolar plants due to the high enthalpy of the hydrogenation-dehydrogenation reactions (Perejón et al., 2016). Moreover, magnesium has a relatively high abundance in earth. The kinetics of the dehydrogenation hydrogenation reaction plays an important role for these two applications. Table 2.1 shows some of the properties of magnesium hydride:

Table 2.1: Properties of magnesium hydride (MgH_2)

Molar mass	26.3209 g/mol
Density	1.45 g/cm³
Specific heat capacity	35.4 J/mol K
Standard molar entropy	31.1 J/mol K
Standard entalphy of formation	-75.2 kJ/mol K
Gibbs free energy	-35.9 kJ/mol K

The main disadvantages of MgH_2 as a hydrogen store is the high temperature of hydrogen discharge, slow desorption kinetics and a high reactivity toward air and oxygen (Sakintuna et al., 2007). Thermodynamic properties of the magnesium hydride system have been investigated by (Bogdanović et al., 1999). The results showed high operating temperature which is too high for practical on-board applications (Bogdanović et al. 1999).

Magnesium hydride has high thermodynamic stability which results in a relatively high desorption enthalpy.

The MgH_2 solid has a tetragonal structure of rutile type, specified by a lattice parameter *a* and the *c*/*a* ratio (Pozzo, 2008). Figure 2 shows Crystal structure of MgH_2. The Mg and H atoms are represented, respectively, by light blue and dark red colors (Pozzo, 2008).

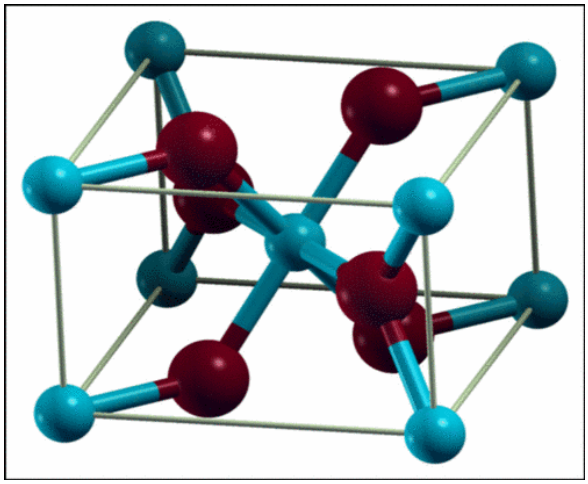


Figure 2: (Pozzo, 2008).

2.3.2 Titanium Hydride

Titanium hydride is well known for its stability in air because of formation of thin TiO_2 oxide layer on top of TiH_2 powder particles. This formation of the oxide layer is usually related to high affinity of titanium to oxygen. This oxide layer also can be formed only in few seconds on top of TiH_2 particles in low vacuum. Besides that, the range of the thickness of TiO_2 layer that is formed on the titanium hydride layer is in the range of 130 nm. Existence of oxide layer on top of powder particles was confirmed with AES, XPS and EDXS cross section line scans (Paulin et al., 2012).

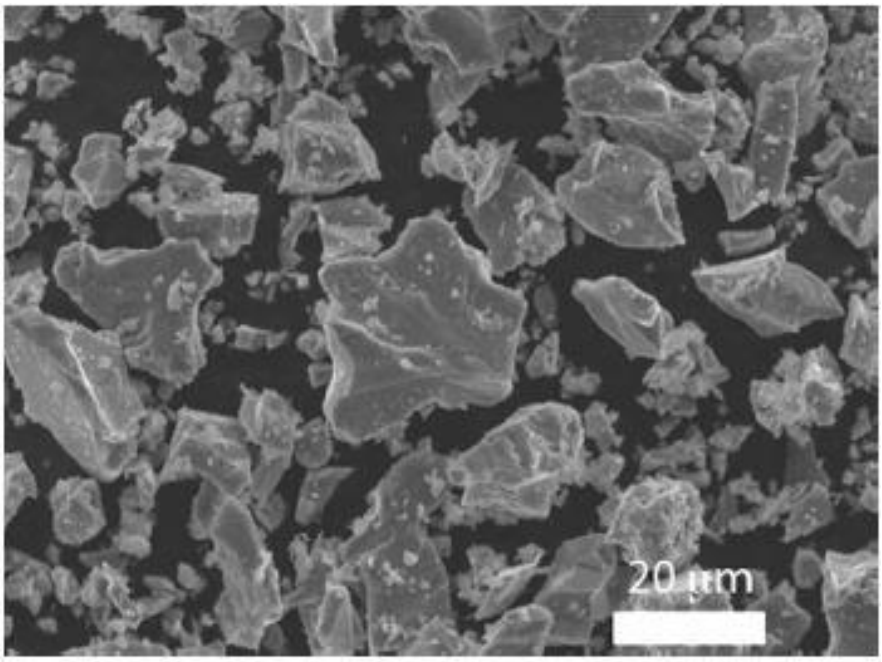


Figure 2.1: SEM image of titanium hydride powder (Paulin et al., 2012)

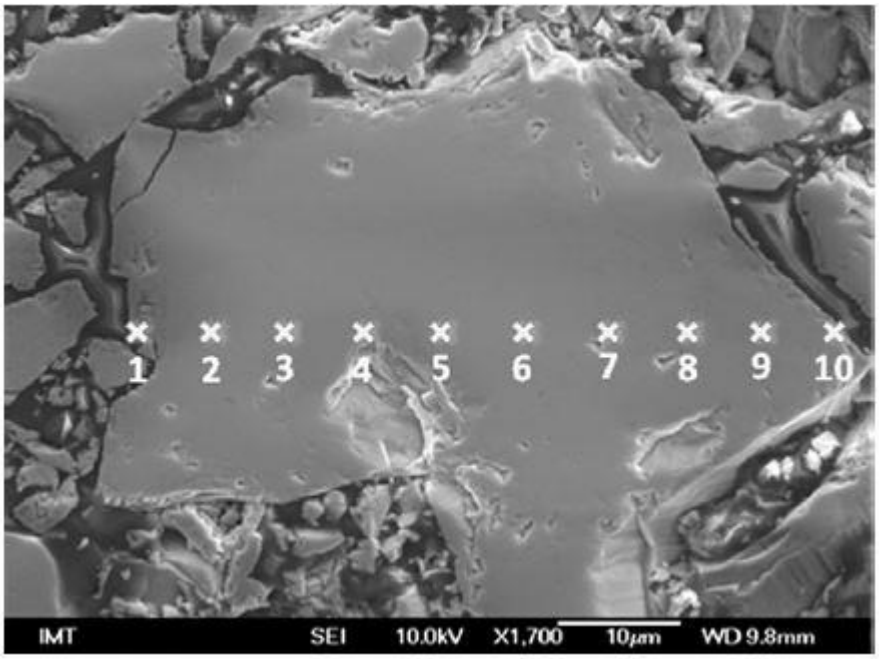


Figure 2.2: SE image of EDXS line analysis spots on cross section TiH_2 powder particle (Paulin et al., 2012)

In the research done by (Paulin et al., 2012), scanning electron microscopy images was done with the FE-SEM JEOL JSM-6500F field emission scanning electron microscope. Energy dispersion spectroscopy (EDXS) also being performed with the Inca Energy 400 EDXS analyser. TiH_2 powder was fixed to carbon tape on the SEM holder for SEM imaging. For SEM process, images were made at 15 kV and with various magnifications, and they are shown in Figs. 2.1. $TiH2$ powder for the EDXS line analysis was prepared as for standard metallographic specimens: hot mounted into Bakelite and then ground and polished (Paulin, et al., 2012).

Titanium hydride (TiH_2) acts as an excellent catalyst in reversible dehydrogenation of other hydrides and carbon nanotubes (Kumar et al., 2007). Besides that, TiH_2 is also can be used as a bonding material to attach the diamond surface to metals (Kamiya et al., 2006). There are many applications of titanium hydride such as, it can act as a catalyst in preparation of titanium compounds, as a source of pure H_2, for the formation of ceramic and glass seals from a mixture of active metal titanium or titanium hydride in powder form and titanium coatings. TiH_2 exhibits tetragonal structure at ambient conditions with wide range temperature stability compared to other metal hydrides (Zhang, 1997).

Titanium hydride is formed by reaction of titanium with hydrogen, Ti(s) + H_2(g) = TiH_2(s). Rapidly synthesized titanium hydride in room temperature by ball milling titanium powders in a hydrogen atmosphere. Hydrogenation process is a process which the formation of titanium hydrogen solid solution and followed by the formation of titanium hydride. The hydride that is formed by the milling process, has lower initial and final temperatures of dehydrogenation and a slightly narrower temperature range of dehydrogenation in comparison with a hydride that is prepared by standard methods (Zhang, 1997).

2.3.3 Titanium Hydride Production

Titanium hydride powder that were produced will be counted as success if it has some criteria such as the availability of low-cost but high-quality titanium hydride powder. However, conventionally titanium hydride powder is being produced by hydrogenation of low-grade titanium sponge, turnings, and other titanium materials (Duz et al., 2016). Production of hydrogenated titanium alloy is based on hydrogenation of already produced titanium materials. Hence, its cost must be higher than those of the primary titanium products. In order to meet the requirements of low-cost raw material, the titanium hydride powder that are being produced is better be less expensive or at least have the equal cost compared to the primary titanium products.

ADMA Products, Inc. in cooperation with PNNL and Ukrainian partners (Institute of Titanium and IMP) has developed a new approach for manufacturing the hydrogenated titanium (Ivasishin et al., 2015). The integration of titanium production and its hydrogenation in one continuous cycle, including reduction of $TiCl_4$, vacuum distillation, and hydrogenation of the sponge block in the same vessel upon cooling from the distillation temperature are some of the key features of this research. All these key features help to make this process different from normal operations of removing the titanium sponge block from the vessel at the end of the reduction cycle, crushing of the block, and, finally, performing hydrogenation of crushed sponge in another vessel.

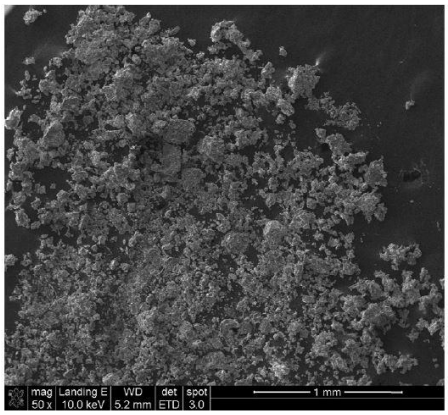
ADMA Products, Inc. also accomplished further developments of titanium hydride powder manufacturing process (Klevtsov, A et al., 2013). Figure 2.3 shows how the reaction of magnesium–hydrogen reduction process. This process was proposed as the most cost-

effective approach to produce the low-cost, high-quality titanium hydride powder (Duz et al., 2016). In this process, hydrogen which act as a reducing agent is replacing magnesium.

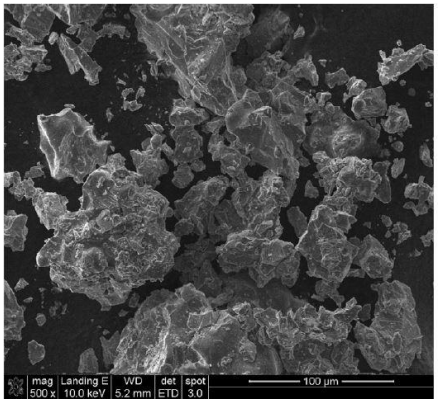
$$TiCl_4 + H_2 + Mg \rightarrow TiH_2 + MgCl_2$$
$$TiCl_4\ (gas) + H_2\ (gas) \rightarrow TiCl_3\ (solid) + HCl\ (gas)$$
$$TiCl_3\ (solid) + Mg\ (liquid) \rightarrow Ti + MgCl_2$$
$$HCl\ (gas) + Mg\ (gas) \rightarrow MgCl_2\ (liquid) + H_2\ (gas)$$
$$Ti + H_2\ (gas) \rightarrow TiH_2$$

Figure 2.3: Chemical reaction of hydrogen during reduction of titanium (Duz et al., 2016)

In this reduction stage, hydrogen is playing important roles which is significantly shortens successive vacuum distillation stage and allows lower distillation temperature. In this process, distillation is done in such a way that hydrogenation or dehydrogenation steps. This could be resulting in a highly developed porosity and cracking due to an 18% difference in titanium and titanium hydride densities (Duz et al., 2016). Figure 2.4 shows the micrograph of titanium hydride powder averaged from 25 lots produced by ADMA process.



(a)



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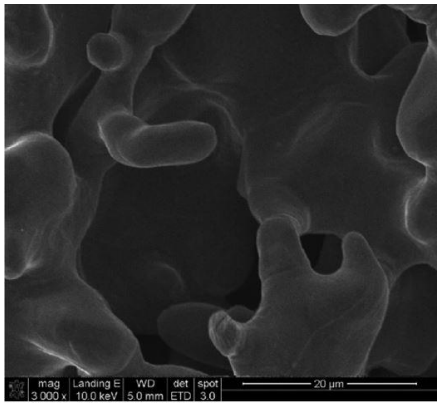

(c)

Figure 2.4: Micrograph of titanium sponge and titanium hydride powder with different magnification (a) 50x, (b) 500x and (c) 3000x

2.4 Kinetic Model

Kinetic modelling of a simple compound inside and outside really important to be understand very well since it help to understand the complex nature of reaction. Each of every material has different reaction mechanism.

2.5 Particle Gas Reaction System

It is very important to study a simple system before complex system. Hence, it is convenient to start with a single particle reacting with a moving stream of gas, hence a particle-gas reaction system. It can be assumed that a simple reaction:

$$aA(g) + bB(s) \rightarrow cC(g) + dD(s)$$

Where a, b, c and d are the respective stoichiometric coefficient.

This also can be adapted to the interested reaction in this project:

$$MgH_2 + TiCl_4(g) \rightarrow TiH_2 + MgCl_2 + H_2(g)$$

There are many steps in a reaction. All of these steps can be split into several steps which are:

1. Diffusion of gaseous species to the surface.

2. Absorption at the surface of the solid particle

3. Reaction with the solid and formation of gaseous phase

4. Desorption from the surface

5. Diffuse away from the surface.

Furthermore, for endothermic or exothermic reaction, the diffusional and reaction steps will also be accompanied by:

I. Convective heat transfers between the gas stream and the surface of solid particles.

II. Conductive heat transfers within the solid reactant-product matrix (Szekely, 2012).

Figure 2.4 shows a typical diffusion and conduction activities happened for a single particle.

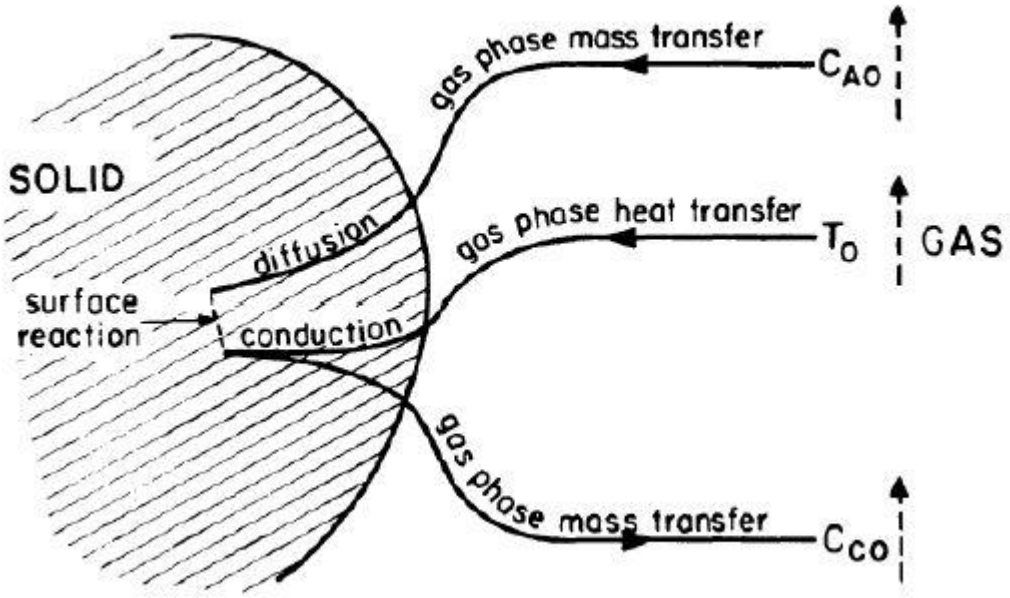

Figure 2.4: Reaction of single solid particle with a moving stream of gas (Szekely, 2012)

Some elements that play important roles towards the system reactions are:

I. Heat and mass transfer.

II. Structural changes of the particles during reaction.

III. Diffusion regime through the pores.

2.5.1 Heat and Mass Transfer

Transferring of the reactant and product into and out of the reacting pallet respectively is the meaning of mass transfer. Hence, it is very necessary to understood more on how the mass is transferred since the speed of the overall reaction is dependent on it. In this project, the main mass transport is the diffusion of titanium tetrachloride gas to the reaction front, as well as the removal of product, titanium hydride from the reacted shell. Sherwood Number which also can be expressed in the function of Reynold Number and Schmidt Number is the mass transfer coefficient in this research. (Gower, 1971).

$$Sh=2.0+(Re^{1/2} \times Sc^{1/2}) \qquad (2.7)$$

One of the important aspect that needs to be well taken care in the modelling of reaction kinetic is heat transfer. If the temperature change is slightly high, the temperature of the reactant and also the incoming reacting gas temperature change. There are many ways that heat can be transported but in this research there are only two ways which are convective and conduction. Nusselt Number and Prandlt Number are coefficients that play an important role. They are important to relate the mass transfer phenomenon to the reaction time needed. Respective calculation for these coefficients are shown in Chapter 4, calculation for both coefficients are well shown.

2.5.2 Structural Change

Structural change is the result of chemical changes in the solid. Some of the possible chemical reactions are softening, sintering, swelling and cracking (Szekely 2012). The reaction and heat transfer process could lead to structural change. In shrinking core model,

pseudo steady state assumption is made. However, in the real life case the structure changes from time to time and leads to changes in many parameters. Generally, this structural changes can be categorized into two categories:

I. Reaction that leads to larger pores and increased porosity.
II. The reaction densifies the body, which leads to a closed pore.

As mentioned earlier, some of the possible chemical reactions that lead to the structural changes are:

I. Swelling
II. Cracking
III. Sintering
IV. Softening

Swelling can be determined as the expansion of the pallet upon heating or during the reaction takes place. This swelling phenomenon happens because of the whisker which is formed from the nucleation of the reduced iron oxide pushes each other. This will cause the pallet to swell. This is a common problem of the iron pallet produced by iron blast furnace.

Meanwhile, cracking might occur during the reaction of the pallet. Extra diffusional resistance that is due to the stagnant film that stays inside the narrow channel will occur during cracking of the pallet. Besides that, the rate of reaction is also will increase since the additional exposed surface for reaction also increase.

Next is sintering which can be explained as a process which a porous compact increases its density when the heat applied is right below its melting point. When the density of the pallet increase, the thermal conductivity is also increase. This is because the reduction of lower thermal conductive phases, such as the gas phase upon sintering. There are many mechanisms for the sintering process such as:

I. Vicious/plastic flow,
II. Evaporation and condensation,
III. Volume and surface diffusion.

According to (Szekely, 2012), all of these mechanisms will become the factor of coarsening of the grain or densification of the body. The coarsening of the grain may lead to a huge change in the thermal conductivity.

Furthermore, softening process can be determined as the extreme form of sintering. The mechanical strength of the pallet will be decrease if near melting point temperature is applied for a prolonged duration hence the pallet being softened.

2.5.3 Diffusion of Mass

One of important phenomenon that occurs during the reactions of a porous solid with gas phase is diffusion process. During reaction, the product diffuses through the pores to the moving stream of gas and transported away. If pore is small enough, the diffusion regime transforms from free collision to Knudsen diffusion. This is according to (Szekely, 2012), small pore size which is comparable to the mean free path of the gas particle therefore it collides more frequently to the wall of the pore rather than the free collision. In Figure 2.4, it shows the Knudsen diffusion along a cylindrical pore.

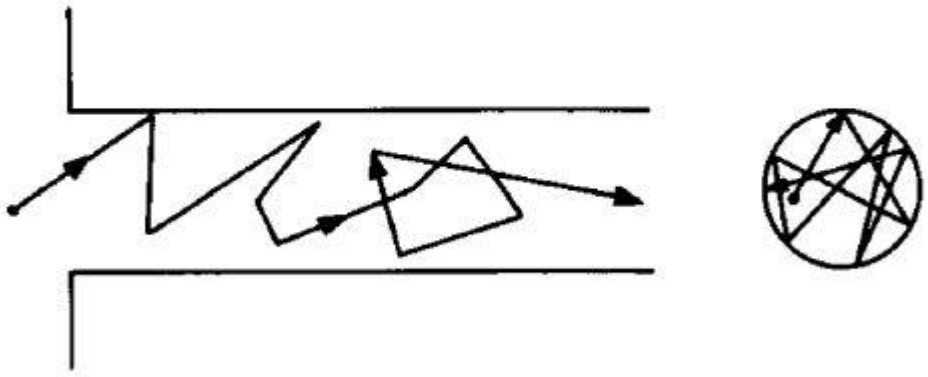

Figure 2.6: Knudsen diffusion in cylindrical pore (Harriott, 2002)

From Figure 2.6 above, it can be seen that the diffusion path length is approximately the same as the diameter of the pore and the direction for both diffusions are random.

Furthermore, in real life situations it is very hard to study the diffusions. Some factors are:

I. The volume occupied by the solid is unknown

II. The diffusion path doesn't follow straight line, but will be quite tortuous instead, colliding with the pore

III. Knudsen diffusion may dominate the diffusion regime

IV. Pressure gradient may exist and assist the diffusion of the species, which has to be taken into consideration also.

In the real world practice, effective diffusivity is used as a replacement for binary diffusivity. The effective diffusivity typically already takes care of the above-mentioned problems and hence it has a lower value than the binary diffusivity (Szekely, 2012).

2.6 Gas-Solid Reaction Model

As stated by (Missen et al., 1999), gas-solid reaction represents the reaction between a solid phase and a moving gas stream, which is a very common reaction can be seen in industry. In general, there are two types of solid and gas phase reaction:

I. Solid reacted with gaseous compound and new solid phase is formed or solid reacted with gas phase compound.
II. A new gas compound is formed.

In this research, only Shrinking Core Model chosen and will be analysed even though there are many models that had been recommended to understand the reaction between a gaseous species and solid particles.

2.6.1 Shrinking Core Model

By assuming a pallet with certain radius and it contacts with a flowing stream and also the gas concentration doesn't change throughout the reaction and the pallet react with it to produce a porous 'ash' is the essence of the shrinking core model according to (Suresh and Sundaramoorthy, 2014). As shown in Figure 2.5, when the reaction between solid and gas is done, it leaves a shell of porous layer which it will cover the unreacted core. As the reaction progress the unreacted core will eventually shrink and hence gets the name 'Shrinking Core Model'. Therefore, if the solid phase is porous, there will be a blurred/gradual transition region between reacted and unreacted region (Albright, 2008)

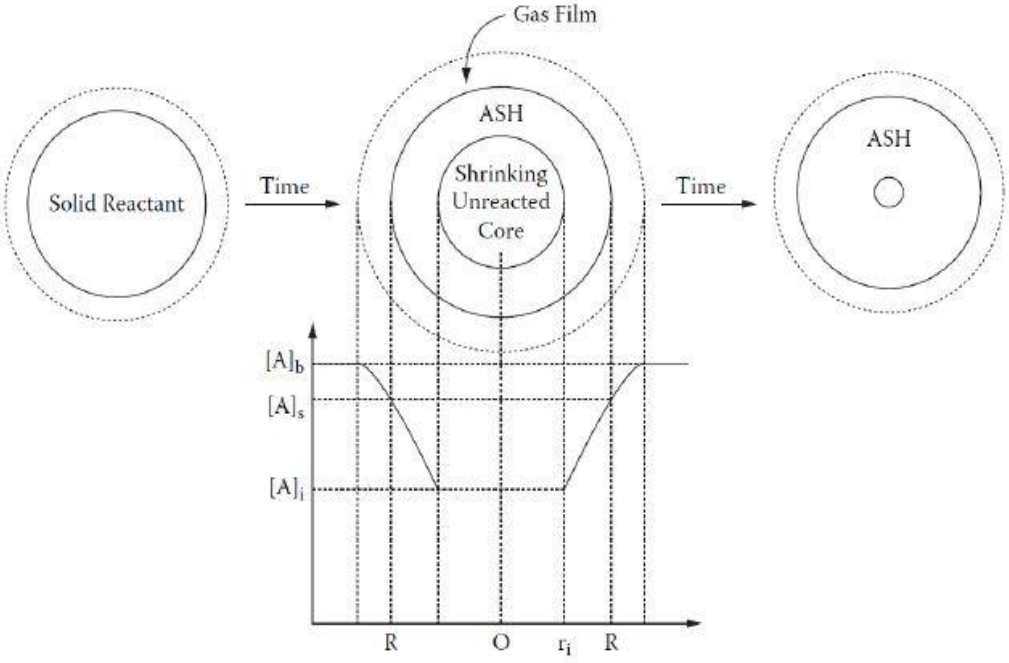

Figure 2.7: Shrinking core model (Albright, 2008)

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter explains more about the preparation of the samples and experimental work that had been carried out. In fact, the relative densities of the produced titanium alloys must be greater than 98% of the theoretical densities. In order to increase the relative densities of the produced titanium alloys, titanium hydride will be used as the starting material. In this experiment, the technique that was used in producing titanium hydride is by reaction between titanium tetrachloride and magnesium hydride technique. This technique was used because of low temperature needed and also low cost.

In this research, the following parameters had been studied: the reaction temperature, the time of the reaction and the chlorine and argon mixture flow rate. Design Expert 8 was used to design this experiment by choosing a full 2^k factorial design. In this method, k represents the total variable and since 3 variables were modified, the total run required would be 8 runs. Besides that, at the center, 3 replications were needed and hence a total of 11 run was done. All the 11 samples were then tested at different reaction temperature (200, 250 and 300 ^{O}C), reaction time (1, 2 and 3 hours) and chlorine and nitrogen mixture flow rate (20, 40 and 60 $cc.min^{-1}$).