Mathematical Modelling of Titanium Hydride Formation from Titanium Tetrachloride with Magnesium Hydride using Matlab

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Abstract. Titanium hydride (TiH₂) is an important material for the synthesis of titanium metal by dehydriding reactions. The reaction to synthesize TiH₂ by reacting titanium tetrachloride (TiCl₄) with magnesium hydride (MgH₂) was investigated so that the important factors governing the kinetics of the reaction could be determined. Experiments were carried out by varying the reaction conditions to establish the optimum level to achieve highest degree of hydriding (Xₘ). The combination of reaction parameters that yielded the highest degree of hydriding (38.49%) was a reaction temperature of 300°C at 180 minutes and Argon (Ar) flow rate of 20 cc/min. The reaction products were characterized using scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) to confirm the formation of TiH₂. The Xₘ was measured by means of weight gain of the sample after the reaction with elemental hydrogen content analysis. Based on the experimental results, the reaction was simulated using Shrinking Core model (SCM) with MATLAB and the kinetic parameters were estimated by fitting the model to the experimental data. The simulated isothermal SCM model achieved an Xₘ of 57% at a reaction time of 180 minutes and Ar flow rate of 20 cc/min. The results of simulation inferred that the isothermal SCM showed good agreement with the experimental outcome providing a good fit to the data. In general, the Xₘ increased with increasing temperature, time and Ar flow rate within the investigated range of parameters.

1. Introduction

The titanium-hydrogen system has generated much attention in battery technology and energy related applications as titanium has been favoured owing to its high capacity of absorbing hydrogen and its ability to be charged to different hydrogen contents [1]. Besides this, the titanium hydride (TiH₂) is gaining attention for the production of Titanium (Ti) metal powder [2]. Titanium is one of the popular metals that can form hydrides, which are non-stoichiometric compounds with tetrahedral distribution of hydrogen atoms randomly distributed in the lattice sites with respect to the titanium atoms [3]. There were many methods to make Ti metal that are racing to replace the Kroll process [4, 5]. Among them were the ADMA [5], oxycarbonitride [6, 7], OS process [8] and TIRO process [9]. The typical procedure to prepare TiH₂ is a traditional method wherein Ti metal is exposed to H₂ at elevated temperature and/or pressure in order to attain the highest hydrogen content [10]. Alternatively, a low cost starting blends of titanium powder and alloying powders (elemental or master alloy ones) were
used for the Blended Elemental Powder Metallurgy (BEPM) method which had relative density lesser than 95% [5]. The benefits of BEPM were minimal material waste and low cost of applications. The development of an innovative and low cost manufacturing non-Kroll process for production TiH₂ powder came as a boon to the Ti industry followed by subsequent improvements [11-13]. This study focus on a new alternative approach of formation of TiH₂ by reacting TiCl₄ with MgH₂ through Eq. (1).

\[
2MgH_2 + TiCl_4(g) \rightarrow TiH_2 + 2MgCl_2 + H_2(g)
\]

\[
\Delta G^\circ \text{ (kJ/mole)} = -0.0393 \times T - 488.42
\]

The preliminary studies on the feasibility and optimized condition to produce TiH₂ through this method has been published elsewhere [2, 13]. In this study, an attempt was made to study the hydriding kinetics of TiH₂ in isothermal condition by means of modelling the solid-gas reaction using Shrinkage Core model (SCM) [14].

2. Methodology

The mathematical model used to compare the kinetics of the hydriding reaction was based on the mass and thermal transport properties of the reactants [15, 16]. Previous application of SCM was limited to Fe₂O₃, TiO₂ and ilmenite systems [17-21]. The kinetic model was developed by using MATLAB software v.2015 with SCM. The transport limited reaction rate of the formation of TiH₂ by using the constructed mathematical models was predicted for isothermal reduction condition. In this study, the reaction started by flowing TiCl₄ gas over MgH₂ which was in a cylindrical pellet form and final product was TiH₂. Details of the experimental setup is given elsewhere [2]. The hydriding reaction was simulated by dividing the pellet into equidistant concentric shells, based on the time taken for each shell to react completely. As the reactants comprise of two different phases, a gas-solid system was considered, wherein complete conversion of MgH₂ into TiH₂ is assumed (Eq. 2). This assumption was valid due to favourable thermodynamic conditions as given in Eq.1.

\[
M(s) + A(g) \rightarrow M(s) + B(g)
\]

where MgH₂ and TiH₂ are denoted by M, TiCl₂ and H₂ gas is denoted as A and B respectively.

2.1 Kinetics of transport model

It is essential to identify the physical and thermodynamic properties of the reactants that affect the kinetics in the system. Among the physical and thermodynamic properties were molecular weight of the species, density, thermal conductivity, emissivity and properties of the gas. The robustness of the model was decided based on the ability of the model to simulate the reaction by involving all the intrinsic and extrinsic parameters that deter the system.

2.2 Determination of core, gas, surface and product temperature

Based on the temperature profiles of the components involved in the reaction in our system as shown in Figure 1., five different temperature zones have been considered for modelling namely, Tg (gas temperature), Tc (core temperature), Ts (surface temperature) and Tp (product temperature). For determining the various assigned temperatures, the system is assumed to be in pseudo-steady state i.e., steady state in a bounded area. It is difficult to predict the variation of temperature in the spherical pellet compared to the gaseous mass transport rate during the reaction. This is due to the fact that heat transfer within the reactant core occurs as a parallel process with the transfer happening through the accumulated solid reaction product and the bulk gas.

\[
(\text{Transfer into region}) + (\text{Transfer out of region}) - (\text{Production within region}) = (\text{Accumulation in region})
\]
In order to simplify expressions of the different temperature zones in MATLAB, a few assumptions were made namely; there was negligible accumulation of heat in the reduction zone, there is only one dimensional heat flow and transfer of heat was conductive, convective and radiative and finally, the average pellet core temperature \( T_c \) represents the overall heat transfer by the pellet. However, in isothermal condition of the reaction system, the temperature changes are constant in the shells. The overall reaction for Eq. (1) of the system was presented by SCM \[14\] and the degree of the hydriding \( X_h \) reaction is predicted by simultaneous solution of the derived equations based on Eq. (3) in MATLAB. A detailed explanation on the solution was given elsewhere \[17, 20\]. The magnitude of \( X_h \) was equated to the fractional reacted \( R' \) in Eq. (4) below.

\[
R_o \rho_{MC} (1 - (1 - R')^{\frac{1}{3}}) = K_{eq} t
\]

Where \( R' \) is the fractional reaction, can be represented by several forms, such as instantaneous pellet weight divided by initial pellet weight or remaining volume divided by the initial volume \( R' = \left( \frac{M_o - M_t}{M_o - M_f} \right) \), \( M_o \) is the initial weight of the pellet, \( M_f \) is the final weight of the pellet, \( M_t \) is the weight of the pellet at time ‘t’ and \( \rho_{MC} \) is the molar density.

3. Results and discussions

Based on the experimental results previous work of Atif Sadaqi \[14\] and Udayakumar et al. \[2\], the optimized conditions for achieving the highest \( X_h \) was chosen. The model was simulated for a combination of two different reaction temperatures namely, 300°C and 200°C at 180 minutes with Argon (Ar) flow rate of 20 cc/min for isothermal condition. The experimental and simulated outcomes for isothermal conditions are individually interpreted and compared to determine the deviation.

3.1 Isothermal shrinking core model

The major assumptions that are made before simulating Isothermal-SCM were; the temperature is homogenous throughout the reaction and also the temperature of the pellet was uniform and constant throughout the reaction. The \( X_h \) determined by simulations using isothermal SCM was shown in Figure 2. It can be seen that as temperature increases, the rate of \( X_h \) also increases. The reaction was expected to be at 50% completed by 180 minutes at temperature of 200°C and Ar flow rate of 20 cc/min according to this model. Furthermore, it can be noted that an increase in 100°C of reaction temperature allowed the reaction to be completed faster by 8%. There were still a few assumptions made in this model stated by Gower \[16\] that were hard to be accomplished in the model namely; the sample was assumed to remain intact throughout the reaction and the pellet porosity was also assumed constant. In reality, it was difficult to model the variations in porosity function as the dehydriding reaction was constantly producing pores from the evolution of H\(_2\) gas. Secondly, the intense exothermic reaction during the formation of TiH\(_2\) as well as the thermal expansion of the sample itself caused the pellet to crack and expose multiple new surface areas. As a result of this phenomenon, the reaction rate could be altered. On the other hand, as the reaction between TiCl\(_4\) and MgH\(_2\) proceeded,
the removal of Mg in the form of MgCl$_2$ occurred which further affected the pellet porosity. This in turn will accelerate the reaction rate which will lead to the deviation of simulation results from experimental.

![Graph of Predicted Degree of Hydriding - Isothermal](image1.png)

**Figure 2.** Isothermal SCM plot of degree of hydriding

![Comparison of Degree of Hydriding Predicted vs. Experimental](image2.png)

**Figure 3.** Comparison of isothermal with experimental data by using the model of SCM.

**Figure 3** shows the comparison of the experimental and simulated outcomes of the hydriding reaction with Ar flow rate of 20 cc/min, reaction time of 180 minutes and for temperatures 200°C and 300°C. On comparing the curves of simulated (isothermal condition) with experimental data, for both temperatures given in **Figure 3**, the reaction does follow the proposed model initially. However, upon reaching a period of approximately 80 minutes, the deviation started to occur. This showed that the experimental results were much more complex than the present model could predict. The reaction trend slowed down and eventually reached a plateau with final $X_h$ indicating a mass controlled mechanism [22].

### 3.2 Confirmation test

In an effort to provide additional evidence to support the validity of the SCM results, experimental results were obtained by using Scanning Electron Microscopy equipped with Electron Dispersive X-ray Spectroscopy (SEM/EDX; Leo Supra 35VP). The SEM/EDX analysis were carried out for reactant products. **Figures 4 and 5** showed the SEM micrographs of the hydrided samples at 180 minutes of reaction time, Ar flow rate of 20 cc/min and reaction temperature of 300°C and 200°C respectively. Although the scope of SEM/EDX analysis was restricted to the surface analysis, it helps to understand the progress of the reaction which can be seen by the presence of Ti metal peaks below 2 eV. For the stability of TiH$_2$, electronic charge on the Ti metal should be between 2 -1.50 eV as evident by the numerous stable phases such as TiH$_2$ - TiH$_{1.5}$. The presence of Ti electron peaks below 2 eV confirms the formation of TiH$_2$ in the reaction products. Furthermore, hydrogen atoms were not detected by EDX due to the limitation of the Leo Supra 35VP instrument. In **Figure 4**, there were numerous needle like structures which corresponded to the Magnesium Oxychloride (MgOCl$_2$) formed as a result of oxygen contamination due to exposure to ambient moisture. XRD analysis as reported by Udayakumar et al. [2] showed that the bulk product consisted of MgCl$_2$, TiCl$_{2.3}$ and TiH$_2$. An irregular cluster of mass can be seen in **Figure 5** which is an agglomeration of the TiH$_2$ and MgCl$_2$ with some unreacted MgH$_2$. The experimental study was done in Ar atmosphere but a low $X_h$ indicate that the mass transfer in Ar atmosphere was low. Further thermodynamic analysis done by Atif Sadaqi [14]
has indicated that H₂ gas atmosphere was more preferred for higher rate \( X_h \). A detailed explanation of the role of H₂ gas was given elsewhere [2].

| Element | Wt.% | At.% |
|---------|------|------|
| O       | 36.52| 49.90|
| Mg      | 43.15| 38.81|
| Cl      | 12.57| 07.75|
| Ti      | 07.76| 03.54|

**Figure 4.** SEM/EDX micrograph of product obtained by hydriding at a reaction temperature of 200°C at 180 minutes with Ar flow rate of 20 cc/min.

| Element | Wt.% | At.% |
|---------|------|------|
| O       | 26.27| 37.21|
| Mg      | 57.80| 53.88|
| Cl      | 08.23| 05.26|
| Ti      | 07.70| 03.64|

**Figure 5.** SEM/EDX micrograph of product obtained by hydriding at a reaction temperature of 300°C at 180 minutes with Ar flow rate of 20 cc/min

4. Conclusion

Shrinking core model (SCM) was used to study the reaction between MgH₂ and TiCl₄ using MATLAB. Results of the simulations were used to compare with the experimental results obtained by previous study on the reaction kinetics [2]. The isothermal SCM gave a \( X_h \) of 57% at 180 minutes with temperature of 300°C with Ar flow rate of 20 cc/min. Isothermal SCM showed considerable approximation to the experimental results. SEM/EDX analysis confirmed the occurrence of hydrides in the reacted products. There were some discrepancies between the predicted and experimental results which could be due to the limitation of SCM to predict variations in porosity and temperature in the concentric shells. All in all, both models followed similar trend with the experimental data. Future hydriding experimental work will be carried out in H₂ atmosphere to increase the \( X_h \) magnitude. In conclusion, the SCM developed provided an insight into the reaction mechanism and rate controlling steps during hydriding of TiCl₄ with MgH₂. These results will pave for innovative ways to synthesize TiH₂.

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