Formation of Titanium Hydride from the Reaction Between Magnesium Hydride and Titanium Tetrachloride

Sanjith Udayakumar¹, Atif Sadaqi¹, Najwa Ibrahim¹, M. N. Ahmad Fauzi¹, Sivakumar Ramakrishnan¹ and Sheikh Abdul Rezan¹*

¹School of Materials & Mineral Resources Engineering, Universiti Sains Malaysia, Engineering Campus, Nibong Tebal, Malaysia

*Email: srsheikh@usm.my

Abstract. The reaction between magnesium hydride (MgH₂) and titanium tetrachloride (TiCl₄) to produce titanium hydride (TiH₂) was carried out at varying temperature, time and Argon (Ar) gas flow rate. The reaction conditions were optimized for increasing the formation of TiH₂ by using the statistical design of experiments (DOE). The hydriding temperature was varied from 200 to 300 °C, while the reaction time was changed from 60 to 180 minutes. The flow rate of argon gas was controlled in the range of 20 to 60 mL.min⁻¹ to minimize TiCl₄ dilution. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), Elemental hydrogen analyzer. From the experiments, the highest weight change (Xₜₜ) of the sample produced at 300 °C for 180 minutes with Ar flow rate of 20 mL.min⁻¹ was 0.19 wt.% and the degree of hydriding (Xₕ) of 38.49% by elemental hydrogen analysis. The DOE analysis inferred that the reaction time was the most significant factor followed by the flow rate of Ar gas and reaction temperature. The SEM/EDX analysis indicated that the product was composed of MgH₂, MgCl₂, TiCl₂.3 and TiH₂. The product contained a minor phase of TiO₂ that could be due to seepage of ambient moisture into the reaction chamber.

1. Introduction

Titanium (Ti) is acknowledged for its strategic importance as it exhibits attractive properties such as low density, high strength and high structural efficiency for critical, high-performance aircraft, such as jet engine and airframe components [1, 2]. There were numerous processing methods to produce titanium (TiH₂) that has been carried out at varying temperature, time and Argon (Ar) gas flow rate. The reaction conditions were optimized for increasing the formation of TiH₂ by using the statistical design of experiments (DOE). The hydriding temperature was varied from 200 to 300 °C, while the reaction time was changed from 60 to 180 minutes. The flow rate of argon gas was controlled in the range of 20 to 60 mL.min⁻¹ to minimize TiCl₄ dilution. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), Elemental hydrogen analyzer. From the experiments, the highest weight change (Xₜₜ) of the sample produced at 300 °C for 180 minutes with Ar flow rate of 20 mL.min⁻¹ was 0.19 wt.% and the degree of hydriding (Xₕ) of 38.49% by elemental hydrogen analysis. The DOE analysis inferred that the reaction time was the most significant factor followed by the flow rate of Ar gas and reaction temperature. The SEM/EDX analysis indicated that the product was composed of MgH₂, MgCl₂, TiCl₂.3 and TiH₂. The product contained a minor phase of TiO₂ that could be due to seepage of ambient moisture into the reaction chamber.
traditional powder metallurgy (PM) approach seemed viable and favourable route for cost effective fabrication of titanium alloys components [1]. The blended elemental powder metallurgy (BEPM) method used low cost starting blends of titanium powder and alloying powders which offers superior mechanical properties. The relative densities of different grades of titanium alloys must be greater than 98% of the theoretical densities in order to achieve a desired level of specific properties such as strength, ductility and creep resistance. However, the relative densities of the titanium alloys produced by powder metallurgy do not exceed 95% [1, 12]. In order to balance the achievable properties of titanium alloys without additional thermo-mechanical operations, the TiH$_2$ was used as the starting material instead of conventional Ti metal powder. TiH$_2$ was being produced by hydrogenation of low-grade titanium sponge, turnings, and other titanium materials until a revolutionary approach called the ADMA process was introduced by Institute for Metal Physics (Ukraine), Incorporated [13]. This process was developed and several improvements have been carried out to produce the low-cost, high-quality titanium hydride powder [14, 15]. In this study, to improve on the ADMA process, a laboratory scale work was conducted to develop a low cost, low temperature process for synthesizing TiH$_2$ powder by means of metallothermic (hydrides of alkali or alkali earth metals) reduction of TiCl$_4$. Previous work on converting titanium dioxide (TiO$_2$) to TiH$_2$ using MgH$_2$ was the starting point for this innovation [16].

2. Experimental Setup

Titanium hydride (TiH$_2$) is produced by the gas-solid hydriding reaction between an alkali earth metal hydride (i.e., MgH$_2$) and TiCl$_4$. The expected chemical reaction is as follows:

$$2MgH_2 + TiCl_4(g) = TiH_2 + 2MgCl_2 + H_2(g), \Delta G^\circ(\text{kJ/mole}) = -0.0393^*T - 488.42 \text{ (kJ/mol)}$$

The value for standard change in Gibbs free energy change ($\Delta G^\circ$) indicated that the reaction was thermodynamically feasible and spontaneous at lower temperatures (<350°C) compared to the conventional ADMA process which takes place between 800-900°C [14]. Argon (Ar) gas was used as carrier gas in the reaction to facilitate the flow of TiCl$_4$ and dilute its concentration. A flow rate meter was used to control the flow of Ar gas that passed through the reaction chamber. The MgH$_2$ pellet was placed in an alumina crucible. The crucible with MgH$_2$ pellet was placed at the centre of the quartz tube at the desired temperature. A hot plate was used to evaporate the TiCl$_4$ liquid into gaseous state at 135°C. The vapour of TiCl$_4$ produced was carried by the Ar gas into the quartz tube for the reaction between MgH$_2$ and TiCl$_4$ to occur. To ensure the molar ratio of TiCl$_4$/MgH$_2$ was below 2, the partial pressure of TiCl$_4$ ($p_{TiCl4}$) vapour was estimated based on work done by Navarro et al. [17]. Residual exit gas was neutralized by NaOH into NaCl before excess Ar was released to ambient atmosphere. The percentage of TiH$_2$ formed was determined based on the gravimetric analysis of the reacted sample and final hydrogen content via elemental hydrogen analyzer (Perkin Elmer Series II CHNS/O analyzer, model 2400). The calculations for degree of hydriding was made assuming full conversion of TiCl$_4$ to TiH$_2$ with no other intermediate compounds formed. The study was carried out by varying three different factors for three distinct levels namely; furnace temperature of 200-300°C, reaction duration of 60-180 minutes and Ar gas flow rate of 20-60 ml.min$^{-1}$. The parameters were chosen based on the dehydriding temperature of MgH$_2$ while reaction time was based previous chlorination study on forming TiCl$_4$ [18, 19]. Design of Experiment (DOE), a statistical approach was used to study of interaction parameters with the measured responses so that the most significant parameters in the reaction can be identified. Besides this, all of the samples and reacted products were analysed by X-ray Diffraction using Cu-K$_\alpha$ radiation (XRD; Bruker D8-advance). XRD was used study the phases present in the reaction products and determine the extent of hydriding in the reaction. The surface morphology and the elemental composition of the sample was
studied by Scanning Electron Microscopy equipped with Electron Dispersive X-ray Spectroscopy (SEM/EDX; Leo Supra 35VP). The degree of hydriding was measured using Elemental CHNS/O analyser by determining the hydrogen content present in the reactants before and after the hydriding process.

3. Result and Discussion

3.1 Characterization of Magnesium Hydride

The SEM/EDX analysis was performed to confirm the elements and ensure that the investigated MgH₂ powder was of high purity. The SEM images (Figure 1) show that the MgH₂ powder had an irregular flaky structure without any signs of particle agglomeration or oxide content [20]. Elemental analysis via EDX confirmed the presence of 100 wt.% of magnesium and hydrogen atoms were not detected due to instruments limitation to detect this element. The XRD pattern of the raw powder was shown in Figure 2. Since the powder was of high purity, the peaks of MgH₂ are very distinct [21, 22] and follow the reference pattern of ICSD 98-010-9357.

| Element | Wt % | At% |
|---------|------|-----|
| Mg K    | 100.00 | 100.00 |

Figure 1. SEM micrograph and elemental analysis of MgH₂ powder

Figure 2. X-ray Diffractogram of raw MgH₂ powder

3.2 DOE Analysis

The results of the factorial design for the hydriding of TiH₂ are shown in the Table 1. The two responses chosen were percent of weight difference gained (wt.%) and degree of hydriding (Xₘ). From the experiments, the highest weight gain change (Xₘₐ) of the sample produced at 300 °C for 180 minutes with Ar flow rate of 20 mL.min⁻¹ was 0.19 wt.% and the Xₘ obtained to be 38.49 wt.% (Run #4). Theoretical weight gained if full conversion of TiCl₄ to TiH₂ was 0.82 wt.%. Model graph analysis using perturbation plots was also performed in order to interpret the experimental results based on factorial model. Figure 3(a) and (b) shows the perturbation plot for both responses which were Xₘ and Xₘ. From the latter figures shown, it can be observed that all the parameters namely temperature, time, and flow rate of Ar gas have a positive impact on Xₘ and Xₘ. This was corroborated by the positive gradient of the perturbation plot for all the factors. From the slopes of all three factors, the time factor showed the highest positive gradient which indicated the most significant parameter.
### Table 1. Percent Weight difference and Degree of Hydriding for DOE Experimental Conditions

| Standard Run | Temperature (°C) | Time (Minutes) | Flow rate of Argon Gas (ml.min⁻¹) | Percentage of weight difference, Xₜ (wt.%) | Degree of hydriding, Xₜ (wt.%) |
|--------------|-----------------|----------------|---------------------------------|------------------------------------------|---------------------------------|
| 1            | 200             | 60             | 20                              | 0.06                                     | 26.01                           |
| 2            | 300             | 60             | 20                              | 0.03                                     | 25.35                           |
| 3            | 200             | 180            | 20                              | 0.1                                      | 30.86                           |
| 4            | 300             | 180            | 20                              | **0.19**                                 | **38.49**                       |
| 5            | 200             | 60             | 60                              | 0.16                                     | 37.32                           |
| 6            | 300             | 60             | 60                              | 0.06                                     | 30.04                           |
| 7            | 200             | 180            | 60                              | 0.06                                     | 28.1                            |
| 8            | 300             | 180            | 60                              | 0.13                                     | 33.64                           |
| 9            | 250             | 120            | 40                              | 0.13                                     | 33.55                           |
| 10           | 250             | 120            | 40                              | 0.06                                     | 28.11                           |
| 11           | 250             | 120            | 40                              | 0.06                                     | 28.1                            |

**Figure 3.** Perturbation plot of (a) Percentage of weight difference, Xₜ (b) Degree of hydriding, Xₜ

A = Temperature (°C), B = Time (Minutes), C = Flow rate of Argon Gas (ml/min)

#### 3.3 Phase Characterization of Residual Product

The reaction products were characterized to identify and confirm the expected phases formed during the hydriding process. Of all the reactions listed in Table 1 as per the factorial design, experiment designated standard run #4 showed the highest Xₜ. For this sample, the morphology, X-ray diffraction pattern was shown in **Figure 4**. The XRD of the product obtained in Run #4 (300°C, 180 minutes, 20 ml.min⁻¹) showed a lot of peaks corresponding to MgH₂ in spite of bearing the highest Xₜ. Since there was only a partial reaction with TiCl₄, residual peaks of MgH₂ (ICSD 98-010-9357) were observed. Few peaks of TiH₂ confirmed the presence of hydride formed during the reaction. Traces of TiCl₂.₃ (ICSD 98-000-3839) were observed which is due to the low partial pressure of H₂ (p(H₂)) gas in the system since Ar gas was used. Furthermore, there was reaction between MgH₂ with TiCl₄ to form TiCl₂.₃. From the DOE analysis, it was found that the use of Ar gas will not facilitate the full conversion of TiCl₄ to TiH₂ in the investigated range of parameters. Furthermore, due to the low p(H₂) in the reactor, formation of titanium sub-chlorides was
favourable compared to TiH₂. A review of literature found most hydriding studies was done in H₂ gas atmosphere with pH₂ close to 1 atmosphere or greater [1, 16, 24].

Figure 4. XRD pattern of reaction product (Run #4 - 300°C, 180 minutes, 20 ml.min⁻¹)

4. Conclusions
The reaction parameters for MgH₂ with TiCl₄ gas to form TiH₂ was investigated and it was the first reported study by DOE. The study inferred that, the most significant parameter to affect the Xₜ and Xₖ was reaction time followed by Ar gas flow rate and reaction temperature. The highest Xₜ of 0.19 wt. % with Xₖ of 38.49% was achieved at 300°C for 180 minutes with 20 ml.min⁻¹ of Ar flow rate. From the DOE statistical analysis, reaction time was identified as the most significant parameter on both responses measured, followed by flow rate of Ar gas and reaction temperature. The Xₖ was low in Ar atmosphere due to low pH₂ that was more favourable for the formation of titanium sub-chlorides than TiH₂. This investigation has indicated a high pH₂ close to 1 atmosphere was needed to make TiH₂ formation more favourable through this reaction.

Acknowledgements
The authors gratefully acknowledge the support from Universiti Sains Malaysia (USM) Fellowship Award. This work was financially supported by USM and Ministry of Higher Education (MOHE) of Malaysia through the following research grants: Fundamental Research Grant Scheme (FRGS) (No. 203/PBAHAN/6071364), USM Research University Individual (RUI) grant (No. 1001/PBAHAN/814273) and Nippon Sheet Glass Research Grant (NSGRG) (No. 304/PBAHAN/650360/N120). Special thanks to USM technician, Mr. Azrul for supporting the experimental work.

References
[1] Duz V, Matviychuk M, Klevtsov A, Moxson V 2017 Metal Powder Report 72 30
[2] Van Vuuren DS, Oosthuizen SJ, Heydenrych MD 2011 Journal of the Southern African Institute of Mining and Metallurgy 111 141
[3] Kroll W 1940 Transactions of the Electrochemical Society 78 35
[4] Doblin C, Chryss A, Monch A 2012 Key Engineering Materials: Trans Tech Publ.
[5] Ahmadi E, Yashima Y, Suzuki RO, Rezan SA. 2018 Metallurgical and Materials Transactions B 1-14
[6] Ahmadi E, Fauzi A, Hussin H, Baharun N, Ariffin KS, Rezan SA 2017 International Journal of Minerals, Metallurgy, and Materials 24 444
[7] Reilly JJ, Sandrock GD 1980 Scientific American 242 118
[8] Ivasishin O, Moxson V 2015 Titanium Powder Metallurgy 117-48.
[9] Ibrahim N, Ahmadi E, Rahman SA, Fauzi MNA, Rezan SA 2017 AIP Conference Proceedings 1805 040005
[10] Ahmadi E, Sereiratana E, Rezan SA, Yeoh F, Fauzi A, Zhang G 2016 Materials Science Forum Trans Tech Publication
[11] Ahmadi E, Rezan SA, Baharun N, Ramakrishnan S, Fauzi A, Zhang G 2017 Metallurgical and Materials Transactions B 48 2354
[12] Ivasishin O, Moxson V 2015 Butterworth-Heinemann 117-48
[13] Froes FH 1998 JOM 50 41
[14] Klevtsov A, Nikishin A, Shuvalov J, Moxson V, Duz V 2013 Adma Products, Inc., assignee. United States patent US 8 388,727
[15] Kasparov SA, Klevtsov AG, Cheprasov AI, Moxson VS, Duz VA 2011 Adma Products, Inc., assignee. United States patent US 8 007,562
[16] Fang ZZ, Middlemas S, Guo J, Fan P. A 2013 Journal of the American Chemical Society 135 18248
[17] Navarro RCS, Vasconcellos ET, Brocchi EA 2017 Thermochimica Acta 647 22
[18] Ahmadi E, Hamid SARBSA, Hussin HB, Baharun SRNB, Ariffin KSB, Fauzi M 2016 International Journal of Jaipur National University 5 11
[19] Ramakrishnan N, Kwok TC, Hamid SARSA 2016 AIP Conference Proceedings
[20] Itam Sulaiman N, Juahir N, Mustafa N, Halim Yap FA, Ismail M 2016 Dalton Transaction 45, 19380
[21] Phetsinorath S, Zou J-x, Zeng X-q, Sun H-q, Ding W-j 2012Transactions of Nonferrous Metals Society of China 22 1849
[22] Yao M, Chen L, Rao G, Zou J, Zeng X, Peng 2013 J Journal of Nanomaterials 8
[23] Beattie SD, Setthanan U, McGrady GS 2011 International Journal of Hydrogen Energy 36 6014
[24] Zhang Y, Fang ZZ, Xia Y, Huang Z, Lefler H, Zhang T 2016 Chemical Engineering Journal 286 517