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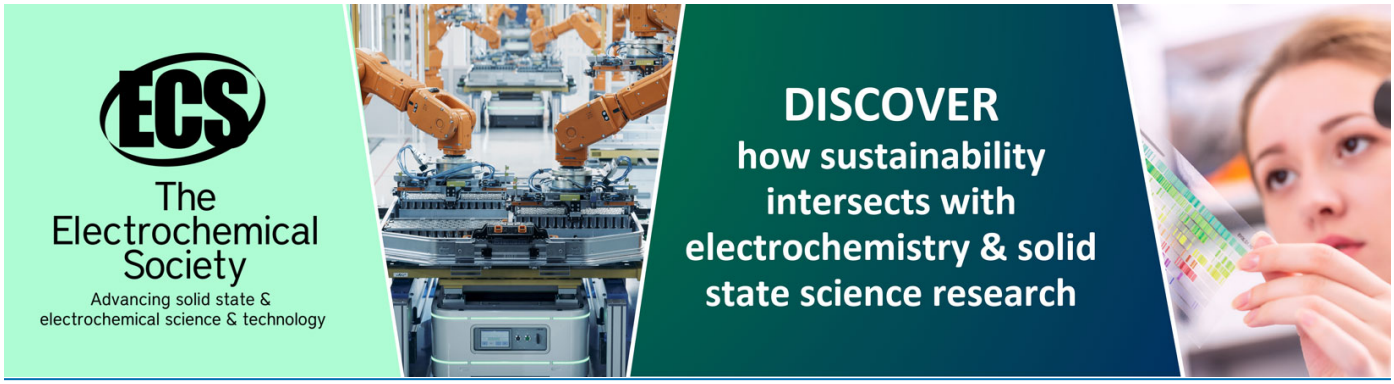


Formation of Titanium Hydride from the Reaction Between Magnesium Hydride and Titanium Tetrachloride

Sanjith Udayakumar[1], Atif Sadaqi[1], Najwa Ibrahim[1], M. N. Ahmad Fauzi[1], Sivakumar Ramakrishnan[1] and Sheikh Abdul Rezan[1*]

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

*Email: srsheikh@usm.my

Abstract. The reaction between magnesium hydride (MgH_2) and titanium tetrachloride ($TiCl_4$) to produce titanium hydride (TiH_2) was carried out at varying temperature, time and Argon (Ar) gas flow rate. The reaction conditions were optimized for increasing the formation of TiH_2 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 $TiCl_4$ 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 (X_w) 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 (X_h) 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 MgH_2, $MgCl_2$, $TiCl_{2.3}$ and TiH_2.The product contained a minor phase of TiO_2 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 Ti metal that include the Kroll [3], TiRO [4], OS process[5] and oxycarbonitride process [6]. This transition element is being widely studied to be exploited in the energy sector as the next generation power source as it has high hydrogen storage affinity as TiH_2 and can be tailored to have different hydrogen concentration depending upon the nature of processing [7]. Though this metal hydride hold promise for clean energy storage, the cost of producing Ti by conventional ingot technology was considerably high due to costly batch manufacturing via the industry standard Kroll process and intricate processing steps [2]. Since there were numerous applications for $TiCl_4$, a titanium by-product from the Kroll process, a coordinated approach to utilize $TiCl_4$ in the production of TiH_2 was attractive [8]. Furthermore, a sustainable and low temperature method to produce $TiCl_4$ has been introduced [9-11]. In the pursuit to lower the production cost, a

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:

$$2MgH_2 + TiCl_{4(g)} = TiH_2 + 2MgCl_2 + H_{2(g)},\ \Delta G°(\text{kJ/mole}) = -0.0393*T - 488.42\ (\text{kJ/mol}) \qquad (1)$$

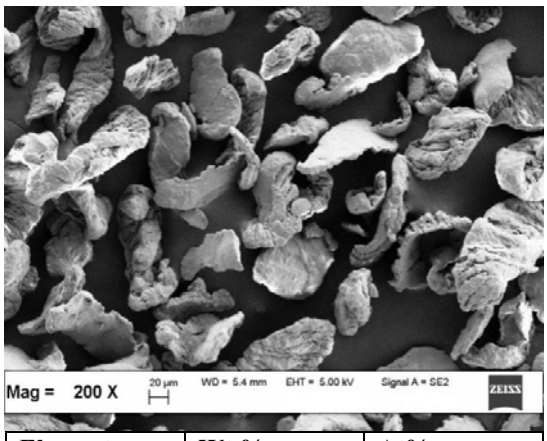
The value for standard change in Gibbs free energy change ($\Delta G°$) indicated that the reaction was thermodynamically feasible and spontaneous at lower temperatures (<350°C) compared to the conventional ADMA process which takes place between 800-900°C [14]. Argon (Ar) gas was used as carrier gas 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_α 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 MgH_2 powder was of high purity. The SEM images (**Figure 1**) show that the MgH_2 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 MgH_2 are very distinct [21, 22] and follow the reference pattern of ICSD 98-010-9357.



Element	Wt %	At%
Mg K	100.00	100.00

Figure1. SEM micrograph and elemental analysis of MgH_2 powder

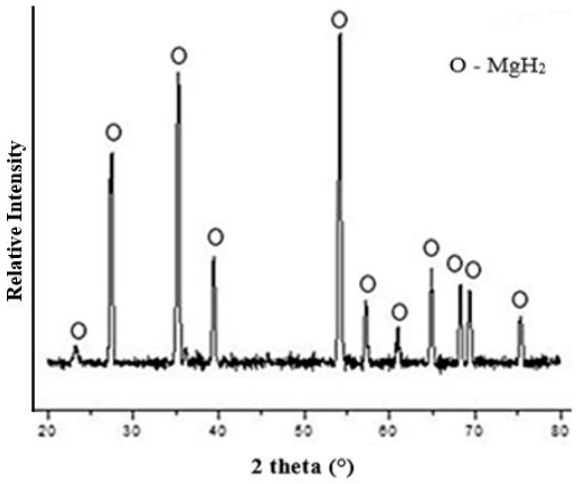


Figure 2. X-ray Diffractogram of raw MgH_2 powder

3.2 DOE Analysis

The results of the factorial design for the hydriding of TiH_2 are shown in the **Table 1**. The two responses chosen were percent of weight difference gained (wt.%) and degree of hydriding (X_h). From the experiments, the highest weight gain change (X_w) 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 X_h obtained to be **38.49 wt.%** (Run #4). Theoretical weight gained if full conversion of $TiCl_4$ to TiH_2 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 X_w and X_h. 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 X_w and X_h. 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, X_w (wt.%)	Degree of hydriding, X_h (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

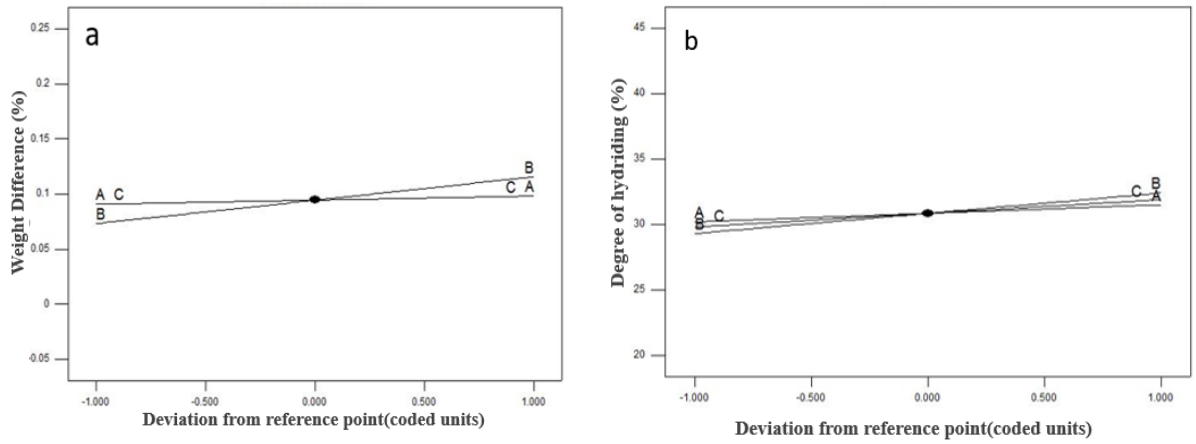


Figure 3. Perturbation plot of (a) Percentage of weight difference, X_w (b) Degree of hydriding, X_h
A = Temperature (°C), **B** = Time (Minutes), **C** = Flow rate of Argon Gas (ml/min)

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 X_w. 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 MgH_2 in spite of bearing the highest X_w. Since there was only a partial reaction with $TiCl_4$, residual peaks of MgH_2 (ICSD 98-010-9357) were observed. Few peaks of TiH_2 confirmed the presence of hydride formed during the reaction. Traces of $TiCl_{2.3}$ (ICSD 98-000-3839) were observed which is due to the low partial pressure of H_2 (p_{H2}) gas in the system since Ar gas was used. Furthermore, there was reaction between MgH_2 with $TiCl_4$ to form $TiCl_{2.3}$. From the DOE analysis, it was found that the use of Ar gas will not facilitate the full conversion of $TiCl_4$ to TiH_2 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 TiH_2. A review of literature found most hydriding studies was done in H_2 gas atmosphere with p_{H2} close to 1 atmosphere or greater [1, 16, 24].

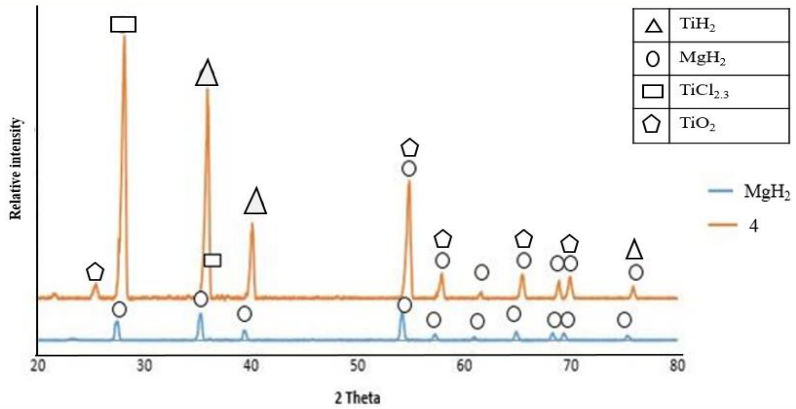


Figure 4. XRD pattern of reaction product (Run #4 - 300°C, 180 minutes, 20 ml.min^{-1})

4. Conclusions

The reaction parameters for MgH_2 with $TiCl_4$ gas to form TiH_2 was investigated and it was the first reported study by DOE. The study inferred that, the most significant parameter to affect the X_w and X_h was reaction time followed by Ar gas flow rate and reaction temperature. The highest X_w of 0.19 wt. % with X_h 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 X_h was low in Ar atmosphere due to low p_{H2} that was more favourable for the formation of titanium sub-chlorides than TiH_2. This investigation has indicated a high p_{H2} close to 1 atmosphere was needed to make TiH_2 formation more favourable through this reaction.

Acknowledgements

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