To my parents, Gab-Soo Jeon and Young-Hee Lee; and my younger sister, Eun-Jung
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The objective of this study was to investigate the hydrogen absorption kinetics and capacity of Mg-nano Ni composites. A dry particle coating technique (Theta Composer) was utilized for coating magnesium particles with nano-Ni. Subsequently, hydrogen absorption and desorption kinetics were evaluated by varying system parameters (i.e. coating time, catalyst loading, coating speed and heating rate). Hydrogen absorption curves plotted as a function of time showed that composites processed for longer periods of time exhibited significantly higher absorption rates. With increased coating time, the catalyst was more evenly distributed over the Mg surface, resulting in a product with increased hydrogen capacity and kinetics. A change in the rate limiting mechanism from the interfacial growth of MgH₂ to diffusion into the Mg particle was observed.

SEM/TEM characterization verified that magnesium hydride forms from the surface rather than from random nucleation and growth in Mg. An analytical model based upon the shrinking core concept was developed to evaluate the dependence of hydrogen absorption on two important rate limiting mechanisms: diffusion and the interfacial growth of MgH₂. Hydrogen absorption capacity was expressed as a function of temperature, hydrogen pressure and Mg.
particle size at the given hydrogenation time. The analytical solution agreed very well with the experimental data for magnesium hydride formation.

A high speed orbiting ball media (HSOBM) processor was developed and utilized to fabricate flake-shaped materials (thin metal flakes with large diameters). Several aspects of flake characteristics produced by the process were studied, including: flake diameter, thickness, morphology (as a function of processing time), ball media count and weight loading. Improvement in hydrogen storage kinetics and capacity of Mg by this novel approach utilizing high aspect ratio powders coated with Ni nanocatalysts was evaluated. The Mg flakes were fabricated by the HSOBM process and were coated with Ni nanocatalysts using the Theta Composer. The flakes thus produced possess more favorable hydrogen absorption/desorption characteristics and improved hydrogen storage capacity than spherical particles. Hydrogen absorption kinetics was identified to be more sensitive to variations in geometric shape as opposed to changes in grain size.
CHAPTER 1
GLOBAL INTRODUCTION

Over the past decade, the looming energy crisis and the concern about the effects of fossil fuel emissions on global warming have created a necessity for cleaner energy options (Dresselhaus and Thomas 2001). Among these, hydrogen has received particular attention as a potential solution to future energy needs (DOE 2003). The use of hydrogen as an alternative fuel in fuel cells has been of interest to many applications, from mobile electronics to aerospace industries (DOE 2007; NASA 2006; Schlapbach and Züttel 2001). Hydrogen fuel cells have the potential to revolutionize the way we power the world by offering cleaner and more-efficient alternatives to gasoline and other fossil fuels (DOE 2007a).

The primary benefit of using pure hydrogen as a power source is that it produces only water vapor and waste heat as exhaust (DOE 2007a; Schlapbach and Züttel 2001). Pure hydrogen can be obtained from the decomposition of methane, coal, liquid petroleum or biomass, via thermolysis, or from the electrolysis of water (DOE 2007a). However, providing a safe, efficient, reliable, and continuous source of hydrogen to a fuel cell still remains a significant technological obstacle.

For light duty automotive vehicles using fuel cells with a driving range greater than 300 miles required by DOE (DOE 2007a), on-board hydrogen storage is essential. The primary problem with storage in pure form is that hydrogen has a very low volumetric/gravimetric storage density (Schlapbach and Züttel 2001; Züttel 2004). If hydrogen is stored as a liquid in a cryogenic tank or as a gas in a pressurized tank to counter this problem, the amount of energy that can be stored in the available space on board is small in comparison to gasoline. The energy required to compress the gas is also a serious drawback (Züttel 2004). These issues make hydrogen cars prone to a limited driving range compared to their conventional counterparts.
Thus, it is essential that new hydrogen storage methods possess a high hydrogen storage capacity.

The highest known volumetric storage densities of hydrogen are found in light metal hydrides and alloys (Schlapbach and Züttel 2001; Züttel 2004). Among the various light metals and alloys that are capable of absorbing/desorbing large amounts of hydrogen, magnesium is considered a promising candidate for solid hydrogen storage due to its high volumetric/gravimetric capacity, abundance and low cost (Chalk and Miller 2006; Schlapbach and Züttel 2001; Züttel 2004). The major disadvantages of utilizing pure magnesium, however, are its slow reaction kinetics and the formation of a dense magnesium hydride which impedes prolonged reactions (Fukai 2005; Schlapbach and Züttel 2001). Such critical issues need to be overcome before its practical applications can be realized.

**Transition Metal Catalyst**

Various attempts have been undertaken to chemically improve the kinetics of Mg by utilizing transition metal catalysts such as Ni, V, Fe and Ti (Holtz and Imam 1999; Huot et al. 1999; Iwakura et al. 2002; Iwakura et al. 1999; Jeon et al. 2006; Liang et al. 1998; Varin et al. 2006; Zaluska et al. 1999). The addition of catalysts with high affinities for chemisorption results in H₂ dissociation into hydrogen atoms at the interface of the Mg-Ni composite by lowering the corresponding activation energy (Sandrock et al. 2002; Stillesjo et al. 1993). These hydrogen atoms can diffuse effectively along the grain boundaries of magnesium (Lueking and Yang 2004; Rozanov and Krylov 1997). By adding a small amount of Ni onto Mg surface (Holtz and Imam 1999), it has been demonstrated that the onset temperature for hydrogen absorption can simply be lowered by approximately 170°C.

Several factors have been identified to be influential in hydrogen absorption and desorption kinetics. Holtz et al (1999) highlighted the importance of the effectiveness of
dispersion of catalyst over the surface of magnesium particles. Several studies have reported that a homogeneous distribution of nano catalysts on the metal drastically reduces the activation energy of hydrogen diffusion and results in more rapid formation of metal hydride even in the presence of oxides and hydroxides (Au 2005; Huot et al. 2001; Jeon et al. 2007; Seayad and Antonelli 2004; Zaluska et al. 2001). Alternatively, it should be noted that when hydrogen diffusion was the rate limiting mechanism, Ni wt. % loading showed negligible impact on H₂ absorption rate or capacity (Jeon et al. 2006).

The particle diameter of the catalyst has also been identified as another influential variable. Varin et al. (2006) investigated the effect of Ni particle size (micro, submicron and nano sizes) on the performance of hydrogen absorption/desorption kinetics of 44 μm Mg powder. It was reported that the addition of nano Ni greatly improves the hydrogen absorption/desorption rate compared to micron/submicron size catalysts.

**Mechanical Ball Milling**

Mechanical milling techniques that aim at increasing surface defects and grain boundaries of metal powders enhance diffusion of hydrogen atoms within the metal, leading to increased hydride formation (Doppiu et al. 2004; Holtz and Imam 1999; Huot et al. 1995; Huot et al. 1999; Iwakura et al. 2002; Liang et al. 1998; Revesz et al.; Tessier and Akiba 1999; Varin et al. 2006; Yu et al. 2002; Zaluska et al. 1999). A significant portion of previous research in this approach has focused on conventional mechanical ball milling, vibratory ball milling, and wet milling to produce changes in the microstructure of magnesium particles. The major disadvantages of mechanical ball milling are the prolonged milling times (30- 60 hrs) (Doppiu et al. 2004; Huot et al. 1995; Tessier and Akiba 1999; Yu et al. 2002) and formation of undesirable alloys. Varin et al. (2006) reported that after 20 hrs of milling, formation of Mg₂Ni alloy was observed, which
resulted in lowered hydrogen absorption capacity. In addition, it is challenging to control the shape and qualitative consistency of the product (Hong and Kim 2001; Hong et al. 2000; Yoshinaga et al. 1997). Therefore, the need arises for a new milling system which is capable of reducing grain size without the formation of metal alloys and with significantly reduced operating times.

**Mechanism of MgH₂ Formation**

There have been many experimental studies in recent years to understand the rate-limiting kinetics and absorption capacity of hydrogen storage in alloys (Fukai 2005; Holtz and Imam 1999; Liang et al. 1998; Liang et al. 1999; Orimo and Fujii 1996; Yang et al. 2000). Holtz and Imam (1999) proposed that nucleation of magnesium hydride on the surface of pure magnesium is the initial rate limiting step for absorption of H₂, as initial hydrogenation (i.e. nucleation of MgH₂) takes place only at the active surface of magnesium. As hydrogenation progresses, the hydride layer (semi-impermeable to hydrogen) thickens and expands into the bulk. Diffusion through the magnesium hydride layer is many orders of magnitude slower than other mechanisms (i.e. nucleation of metal hydride or dissociation of hydrogen molecule into two hydrogen atoms) and subsequently becomes the rate-limiting step in the hydrogenation process (Bloch and Mintz 1997; Friedlmeier and Groll 1997; Sastri et al. 1998; Schweppe et al. 1997). However, these studies have not been experimentally verified adequately. In fact, due to the complexity involved in the micro-structural analysis, very few microscopic studies have been done to investigate the formation of magnesium hydride in a particle. On the other hand, the homogeneous nucleation of magnesium hydride taking place in the bulk has been observed under optical micro-structural analysis (Douglass 1975). This contradicts the previously described theories of hydride formation, where it is assumed that hydride forms as a continuous layer from the particle surface. Thus, there is a need for clarity.
Models for MgH₂ Formation

Several empirical or theoretical kinetic models have also been formulated and subsequently fitted with experimental data for describing hydrogen absorption/desorption behavior of metal hydrides (Chou et al. 2005; Friedlmeier and Groll 1997; Ginstling and Brounshtein 1950; Rudman 1979; Saetre 2006). The nucleation and growth model developed by Avrami (Avrami 1939; Avrami 1940; Avrami 1941) is a frequently applied model for describing phase change in solids. In Avrami’s model, the rate-limiting mechanism is random nucleation and the subsequent three-dimensional growth of a new phase within the bulk. Rudman (1979) later extended Avrami’s model to metal–hydrogen systems; the effects of temperature and hydrogen pressure on the kinetics for hydrogen diffusion-limited cases were considered, assuming a constant growth rate of magnesium hydride. The other commonly accepted model for metal hydride formation was proposed by Flanagan (1978), in which hydrogen molecules are adsorbed or weakly chemisorbed on an active metal surface where they then dissociate into hydrogen atoms. These atoms can easily diffuse between the grain boundaries of the pure metal and then finally form metal hydride (Flanagan 1978; von Zeppelin et al. 2002). If diffusion of hydrogen atoms occurs at a fast rate along the grain boundary (i.e. the grain size is small), a metal hydride layer is formed and thickens into a pure metal core (Zaluska et al. 1999). This concept can be best described by “the shrinking-core model” (Levenspiel 1999). Several numerical studies have been conducted based on the shrinking-core model, considering changes in growth rate for a diffusion limited case (Chou et al. 2005; Ginstling and Brounshtein 1950; Rudman 1979; Saetre 2006; Schweppe et al. 1997).

Barkhordarian et al.(2006) reported that their experimental data of the absorption behavior of magnesium catalyzed with Nb₂O₅ were better described by a three-dimensional diffusion controlled shrinking-core model. Gabis et al.(2005) also compared Avrami’s model and
the shrinking-core model with thermal desorption spectrometry (TDS) experiments of metal hydride, and the results showed that the shrinking core model described the kinetics of hydrogen desorption better. However, predictions by both models still deviate from experimental observations, especially during the initial period of the hydrogenation process (Schweppe et al. 1997; Stander 1977). The reason for the deviation stems from the key assumptions of these models that the process is diffusion limited and that the change in rate limiting mechanisms during the process is not considered. Stander (1977) divided kinetics of Mg hydride formation into two steps (nucleation and diffusion) and likewise fitted his experimental data separately for each of these cases as a function of the fraction ($\alpha$) of metal hydride, and reported that the nucleation equation was valid for pure Mg for an upper limit of 0.18 for $\alpha$ (equivalent to a layer of 1.6 $\mu$m MgH$_2$ on a Mg particle diameter of 25 $\mu$m). After the magnesium surface was utilized ($\alpha$ >0.18), a separate equation for diffusion was reported to reproduce experimental data well.

**Objectives**

The objectives of this dissertation research were to investigate hydrogen absorption mechanisms of a Mg-nano Ni composite and to assess the effects of nano catalyst and the geometry of Mg particles on enhancing hydrogen adsorption kinetics and capacity. Both experiments and theoretical modeling were carried out to help achieve the objectives. The dissertation is divided into four chapters (Chapters 2-5). The major content of each chapter is outlined in the following paragraphs:

Chapter 2 - The kinetics of Mg-Ni composites synthesized by a dry coating technique (Theta Composer) were studied. This provides insight into the rate limiting mechanism change between interfacial growth and diffusion as well as the effects of various processing parameters on hydrogenation/desorption kinetics and capacities. The effects of heating rates on hydrogen absorption kinetics were also explored.
Chapter 3 - The behavior of MgH₂ formation in a Mg particle was experimentally identified via micro-structural analysis. A kinetic model based upon experimental observations was developed to investigate the change in the rate-limiting mechanism and kinetics in hydrogen adsorption. The effects of magnesium particle size, initial hydrogen pressure and temperature on hydrogen absorption kinetics were also assessed.

Chapter 4 - A novel milling processor (High Speed Orbiting Ball Milling – HSOBM) was developed to efficiently prepare flake-shaped Mg particles. The milling mechanisms including plastic deformation, particle-particle-welding and flake deformation were examined. The effects of the processing parameters on the milling efficiency and product characteristics were studied.

Chapter 5 - Improvements in hydrogen storage kinetics and capacity were evaluated through the use of high aspect ratio Mg powders (thin metal flakes with large diameters) coated with Ni nanocatalysts. The coating efficiencies of the HSOBM processor and Theta Composer were assessed. The effects of geometry and grain size on hydrogen absorption kinetics were analyzed.
CHAPTER 2
HYDROGEN ABSORPTION/DESORPTION KINETICS OF MAGNESIUM NANO-NICKEL COMPOSITES SYNTHESIZED BY DRY PARTICLE COATING TECHNIQUE

Introduction

Magnesium hydride has been widely studied as a means for effective hydrogen storage due to its several advantages such as light weight, high hydrogen capacity, natural abundance, low environmental impact and low cost (Schlapbach and Züttel 2001). One of the critical problems which limit the wide usage of Mg for solid storage is its absorption and desorption kinetics, which are only feasible at high temperatures (> 650K). To overcome these limitations, past research has attempted to improve the kinetics through ball milling, hydriding combustion synthesis of the bulk magnesium metal, alloying with transition metal catalysts (i.e. Al, Ti, Cr, Fe, Co, Mn, Zr, Zn and Ge) and destabilizing the magnesium-transition metal-hydrogen matrix (Gennari et al. 2002; Li et al. 2000; Liang et al. 1998; Liang et al. 1999; Raman et al. 2002; Varin et al. 2005; Yang et al. 2000). The role of the catalytic transition metal is to dissociate H₂ into H atoms that can be more readily chemisorbed by magnesium (Friedlmeier and Groll 1997; Holtz and Imam 1999; von Zeppelin et al. 2002), thus improving hydrogen absorption and desorption kinetics. The distribution and dispersion of the catalyst over the surface of magnesium particle is a critical factor in affecting hydrogen absorption and desorption kinetics (Zaluska et al. 1999). With the help of the catalyst, the formation of MgH₂ can be achieved and chemisorption becomes the rate limiting mechanism in the initial stage. However, as the reaction proceeds, an impermeable hydride layer develops and diffusion through the layer becomes the rate limiting mechanism (Friedlmeier and Groll 1997; Holtz and Imam 1999). To maximize the kinetics, the duration of the first limiting mechanism should be kept as long as possible.

In addition to adding transition metal catalysts, the hydrogenation rate over those of the bulk material can also be improved by mechanical milling or ball milling. This changes the Mg
microstructure by creating more defects and grain boundaries near the surface as well as making the nanocrystalline structure amorphous (Orimo and Fujii 1996; Zaluska et al. 1999). These fissures serve as passages for hydrogen diffusion, along with improving hydride nucleation and hydrogen atom penetration (Song 1995). Ball milling, the common technique for alloy preparation, requires processing times ranging from a few hours to 30 hours for complete milling (Charbonnier et al. 2004; Chen and Williams 1995; Gao et al. 2005; Lee et al. 2002; Spassov et al. 2005; Yoshinaga et al. 1997). Dry particle coating can be an alternative to ball milling because of its ability to disperse nanoparticles in 60-90 minutes of time duration (Coowanitwong et al. 2003; Pfeffer et al. 2001).

The objectives of this chapter were to determine the absorption/desorption characteristics and hydrogen storage capacity of Ni nanocatalysts coated magnesium prepared by dry particle coating. The following were investigated:

1) The optimal processing conditions of the dry particle coating process (Ni loading, coating time, coating speed, gap size and heating rate) for hydrogen storage
2) The change in the rate-limiting mechanism in hydrogen absorption
3) The effects of heating rate on hydrogen absorption kinetics/capacity

**Experimental Methodology**

**Dry Particle Coating**

Mg-Ni composites were prepared by Theta Composer (Tokuju, Corp.), a dry coating equipment. A schematic diagram of Theta Composer is shown in Figure 2-1. Ten grams of pure Mg powder (Alfa Aesar 44 μm, 325 mesh) and Ni nanoparticles (Argonide 70 nm) were introduced into the vessel while under an argon environment (4.8 grade) in a glove box (Plas-Labs, Inc. Model 855-AC). Because of the potential reactivity of Mg with oxygen in air, an oxygen analyzer (Cambridge Sensotec, Ltd. Rapidox 3000) was used to monitor the oxygen level
in the glove box and pure argon was constantly supplied to the glove box to ensure the oxygen level was lower than 500 ppm.

Two different weight % of Ni nano particles were tested with two coating times of 60 and 90 min. The coating system was tested with rotor speeds of 3600 and 4600 rpm and a fixed vessel speed of 70 rpm. Two rotor-vessel gap sizes of 1.0 mm and 0.5 mm were used. The rotor operates at high revolution while the vessel counter-rotates at a lower speed. Strong compression and shear forces are applied to the particles when they pass through the narrow gap between the rotor and vessel wall (Pfeffer et al. 2001). The rotors and vessel are made of stainless steel in order to maintain an inert environment and prevent chemical reactions. Smaller gap sizes increase the forces on the powders and may affect the microstructure of the powders, in addition to creating more grain boundaries and irregular surfaces (Orimo and Fujii 1996; Zaluska et al. 1999).

**Hydrogen Absorption Test**

Hydrogen absorption studies were performed using a stainless steel chamber. 0.905 g of the Mg-Ni composite was introduced in to the hydrogenation chamber (180 cm³) in a glove box. A schematic of the hydrogenation system is shown in Figure 2-2. Before introducing hydrogen into the system, the hydrogenation chamber was evacuated (-11 psi) with a vacuum pump and argon (4.8 grade) was used to flush the chamber three times. This was done in order to lower any possibility of contaminants (i.e. O₂, CO₂, or H₂O). The chamber was then pressurized with pure hydrogen (high purity grade) to 145 psi. A blank test was performed using the hydrogenation chamber (without sample) to confirm that there were no leaks. The chamber was pressurized to 145 psi with hydrogen at 25 °C, and then the chamber temperature was raised to 300 °C; heating was then removed to allow for cooling. The initial pressure and final pressure, after heating and cooling, at 25 °C were accurate to within 1 % of each other. This confirmed that there was no
leakage during the hydrogenation process. Under normal experimental conditions, runs were controlled to reach 210 °C. The temperature was measured with two thermocouples (Fisher Scientific model 15-078-39, type K) attached to the inside/outside of the chamber; a digital meter (Fisher 15-078-39) was used to display the output. The pressure was monitored using an electronic pressure transmitter (Omega, PX880) connected to a process panel meter (Omega, DP25B-E). Once the chamber was pressurized, heating tape (Omega FGS101-040, 420 Watt) was wrapped around the chamber. A DAQ (data acquisition module, Omega DAQ-55) and software control program was introduced to automatically acquire internal and surface temperatures as well as internal chamber pressure data on a timely basis. External temperature was used by the software program to control the internal chamber temperature.

**Particle Characterization**

The formation of MgH₂ in the Mg-Ni composites before and after the hydrogen absorption test was determined by X-ray diffraction (Phillips XRD APD 3720) with Cu K radiation. This process was controlled by PC-APD software, which was used for all scans. The morphology change of the sample before and after dry coating was investigated with Scanning Electron Microscopy (SEM, JEOL JSM 6335F). Energy dispersive spectroscopy (EDS) was used to determine the dispersion of Ni nanoparticles on the surface of the host (Mg). Desorption studies were performed using a Thermogravimetric Analyzer (TGA 2050, TA Instruments).

**Data Analysis**

During MgH₂ formation, the loss in moles from gas to solid is indicated by the drop of PV/RT values,

\[
n = \frac{PV}{RT}
\]  

(2-1)
where $P$ is pressure, $T$ is temperature, $R$ is the ideal gas constant, $V$ is the volume of the reaction chamber and $n$ is the number of $\text{H}_2$ moles in the chamber. The PV/RT value was utilized to aggregate pressure and temperature effects simultaneously and to compare experimental data with the theoretical value. For an ideal gas without reaction, the $n$ value would remain constant. When calculating the hydrogen absorption capacity, the initial and final pressures at room temperature were used. Experiments were performed to quantify the reaction rate during the hydrogenation process. TGA data were used as a comparison to the PV/RT data calculated. Results in Table 2-1 verify that the calculated data using measured PV/RT values were accurate to within 2% of the experimental data from the TGA. Therefore, this method was used in subsequent analyses.

**Results and Discussion**

**Particle Morphology & Texture Change**

Particle samples were analyzed with SEM for their morphologies. From the image of pure 44 $\mu$m Mg in Figure 2-3, it was observed that Mg had an irregular shape and a broad size distribution. Images of 44 $\mu$m Mg with nano-Ni 2 wt % after milling with Theta Composer did not show observable physical changes in shape or size distribution. However, in Figure 2-4, these coated particles showed well dispersed white spots over the surface (Figure 2-4a) which were not seen in the image of pure Mg. These white spots were determined to be nano-Ni by SEM EDS mapping (Figure 2-4b).

As shown in Figure 2-5, significant changes in surface morphology were observed upon comparison of the pure Mg particles only and those after hydrogenation. After hydrogenation, a gel type texture was observed on the surface of hydrogenated particles due to the formation of MgH$_2$. Figure 2-6 shows XRD patterns of Mg-2 wt % Ni (90 min processing) with different coating speeds of 4600 and 3600 rpm. Although the characteristic MgH$_2$ peaks ($^\circ\theta = 28$ and 36)
were present for both instances following exposure to $H_2$, the presence of Mg verified the formation of an impermeable hydride layer and inability of hydrogen to permeate into the magnesium particle core (Bloch and Mintz 1997; Holtz and Imam 1999). Characteristic peaks for Ni ($\theta = 45, 51, 66$) were also present for all of the materials processed with Ni. There was no evidence of $Mg_xNi_y$ alloys formed in this dry coating process; samples ball milled for long periods of time in prior studies, however, showed these alloy formations (Song 1995).

**Effects of Coating Time and Speed on Hydrogen Absorption**

The effect of processing time on hydrogen absorption was examined by hydriding composites of Mg-2 wt % Ni processed for 60 and 90 minutes while all other parameters were kept the same. Figure 2-7 shows the different absorption behavior (indicated by different slopes) plotted as $PV/RT$ vs. coating time. The absorption rate indicated by the slope is an important parameter for application. In the initial stage of heating, there was a difference between internal and external temperature readings. The data points during this transient period (before 50 min) should therefore be ignored. It was observed that for the material processed for 90 minutes, there was a significant increase in hydride formation over those composites processed for only 60 minutes. A longer processing time was shown to be more effective in distributing Ni onto the Mg powder surface and resulted in an increase in the number of active absorption sites. A shorter processing time might not have sufficiently dispersed agglomerates on the surface, resulting in only localized catalytic enhancement. Extended processing in Theta Composer improved the hydrogen storage capacity and absorption rate for composites with the 2 wt % Ni loading.

The effect of coating speed on hydrogen absorption was investigated with all other parameters (i.e. coating time, Ni loading, and gap size) kept constant. Pressure decay slopes as a function of time for two different coating speeds are shown in Figure 2-8. Hydrogen absorption
curves show two different slopes. Decaying slopes for two different processing speeds (3600 and 4600 rpm) show similar slopes in the domain of constant temperature, (0.17 and 0.20 respectively for Region I, and 0.12 and 0.10 for Region II), an indicative of having the same mechanisms for H₂ absorption. Initially, hydrogen absorbed in Region I shows a steep slope of pressure decay, while in region II, this slope becomes less steep. The transition of the slope from Region I to II implies a change in the rate limiting mechanism from the interfacial growth of MgH₂ to hydrogen diffusion (Bloch and Mintz 1997; Friedlmeier and Groll 1997).

Higuchi et al (1999) reported that hydrogen penetrates to a terminal depth of 30 μm into the Mg surface, if sufficient time is provided. For a spherical particle, this corresponds to a diameter of less than 60 μm. The penetration depth of hydrogen into the Mg-Ni composite synthesized by Theta Composer was calculated using the change of H₂ moles in the chamber following Equation 2-1. The loss of H₂ was translated into the formation of a MgH₂ film on the surface of Mg particles. The relationship between the volumes of pure Mg before and after hydrogenation can be expressed by

\[ V'_{p} = (1 - \frac{H_c}{7.6}) V_p \] (2-2)

where \(V_p\) is the volume of pure Mg in a single particle, \(V'_{p}\) is the volume of pure Mg after hydrogenation and \(H_c\) is the hydrogen capacity (wt%), and 7.6 (wt%) is the theoretical hydrogen capacity of MgH₂. The penetration depth \(h_p\) can then be determined using the following equation

\[ h_p = r_p - \frac{1}{2} \left[ \frac{6}{\pi} V'_{p} \right]^{\frac{1}{3}} \] (2-3)

where \(r_p\) is the radius of the Mg particle (22 μm in this study). For practical applications, it is desired to maximize the use of the interfacial growth limited Region I. Therefore, it is important
to identify the hydride layer thickness. Based on the hydrogen absorption capacity shown in Figure 2-8, the penetration depth into the 44 μm spherical Mg particles synthesized in this study was calculated to be around 3 μm for Region I.

**Effects of Ni Loading and Gap Size on Hydrogen Absorption**

The effects of Ni loading were studied with 2 and 4 wt % Ni. During the initial stage (before 200 minutes) on Figure 2-9(a), the 4 wt % Ni slope showed a steeper curve than that of the 2 wt % Ni. However, as the absorption time approached this point (200 minutes), both curves converged. In the first region where chemical absorption is the rate limiting mechanism (before 200 minutes), higher Ni wt % might increase the number of active absorption sites so increased the reaction rate in that region. A lower Ni wt % loading might not sufficiently cover the surface, resulting in only localized catalytic enhancement. In other words, by increasing the Ni wt % loading, the quantity of hydrogen absorbed by the 44 μm powders was initially enhanced. After the rate limiting mechanism changed from chemical absorption (Region I) to H₂ diffusion into the Mg particle (Region II), however, Ni wt % loading did not affect H₂ absorption capacity, indicating the limitation of the impermeable layer. In summary, chemical absorption rate was improved by the addition of Ni nanoparticles; ultimately, when hydrogen diffusion became the rate limiting mechanism, the capacity had little dependence on the Ni wt % loading.

The effect of rotor and vessel gap size in Theta Composer was examined by hydriding composites of Mg + 2 wt % Ni processed for 90 minutes. As shown in Figure 2-9 (b), initially, the 0.5 mm gap size produced a slightly better hydrogen absorption capacity. As chemical reaction progressed, the hydrogen absorption curves of 0.5 mm and 1.0 mm gap size came closer to each other. It implies that after the rate limiting mechanism changes from chemical absorption to H₂ diffusion into the Mg particle, gap size does not affect H₂ absorption capacity. It should
also be mentioned that some particles in the 0.5 mm gap case were stuck on the vessel wall due to excessive shear forces. This build-up can sometimes cause damages to the instrument and bring handling difficulties, resulting in unevenly processed particles. Hence, the 0.5 mm gap size was not used in other experiments.

**Effect of Heating Rate on Hydrogen Absorption**

The effect of heating rate on the kinetics was investigated. Experiments were performed using Mg-2 wt % Ni after 90 minutes of processing. The chamber was quickly heated (<50 minutes) to 210 °C, which was then maintained for 400 minutes. The same experiment was then repeated at a lower heating rate, which was heated to 210 °C in 120 minutes. It can be seen in Figure 2-10 how the heating rate affected the progress and final extent of reaction. With a higher heating rate, higher reaction kinetics overcomes the diffusion barrier which results in an increase in the rate of both interfacial growth of MgH$_2$ and hydrogen diffusion. This can allow more hydrogen atoms to permeate further into the Mg core, resulting in a greater hydrogen storage capacity. The penetration depth condition in Region I under this condition was calculated to be 4.6 μm, which was larger than the slower heating case (3 μm). The results demonstrate the benefit of a high heating rate without raising temperature.

**Hydrogen Desorption Rates and Capacity**

In previous sections, the varying parameters experimented resulted in trends specific to each parameter. Samples with a longer coating time, a higher coating speed, 2 wt % Ni loading, and 1.0 mm gap size showed better absorption characteristics. Samples with a higher heating rate also showed greatly enhanced absorption trends. TGA data were used to analyze the desorption characteristics of samples; these data are displayed in Figure 2-11. The hydrogen capacities for normal heating rate samples showed little deviation among different coating speeds, Ni loadings, and gap sizes. However, samples processed at 3600 rpm showed an initial desorption
temperature of approximately 220 °C with a steep desorption slope. On the contrary, those samples of 4600 rpm exhibited an initial desorption temperature of approximately 240 °C, with slopes less steep than in the previous instance, indicating stronger hydrogen bonding. Coating time was the other important parameter affecting desorption. A lower coating time showed a significantly lower final hydrogen capacity than a higher coating time. Another important parameter that affected the capacity was the heating rate. A higher heating rate resulted in a product with a much higher final hydrogen capacity (4.82 %) than samples treated at the lower heating rate.

Summary

The formation of magnesium hydride on Mg-Ni composites synthesized by Theta Composer was studied. This provides the insight of the rate limiting mechanism change between interfacial growth and diffusion. The effects of various parameters on hydrogenation/desorption kinetics and capacities were investigated. Based upon the experimental results, a longer coating time in Theta Composer improved the hydrogen storage capacity and absorption/desorption rates for composite with the same Ni loading due to the better distribution of Ni nanocatalysts. It was also observed that there was a change in the rate limiting mechanism of hydrogenation from interfacial growth of MgH₂ to diffusion through the hydride layer into the Mg particle core. The penetration depth for the interfacial growth limited case was approximately 3 μm at the lower heating rate (1.5 °C/min).

A lower Ni wt % loading did not sufficiently cover the surface and resulted in only localized catalytic enhancement. However, after the rate limiting mechanism changed from the interfacial growth of MgH₂ to H₂ diffusion, Ni wt % loading had negligible impact on the H₂ absorption rate and capacity.
In studying the change in gap size, the 0.5 mm gap produced a slightly better hydrogen absorption rate. However, in this case many particles built up on the Theta Composer vessel wall due to excessive shear forces. Therefore, a 1.0 mm gap size is preferred. A higher heating rate (3.7 °C/min) showed a substantial improvement in hydrogen absorption rate and storage capacity; the corresponding penetration depth of interfacial growth limited Region I was 4.6 μm. A lower coating speed resulted in lower initial desorption temperatures and a steeper desorption rate.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Experiment (TGA)</th>
<th>Calculated</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3600x70, Ni 2%, 90 min, 1.0 mm</td>
<td>3.34</td>
<td>3.33</td>
<td>0.37</td>
</tr>
<tr>
<td>4600x70, Ni 2%, 90 min, 1.0 mm</td>
<td>3.20</td>
<td>3.28</td>
<td>2.39</td>
</tr>
<tr>
<td>4600x70, Ni 2%, 60 min, 1.0 mm</td>
<td>2.12</td>
<td>2.09</td>
<td>1.49</td>
</tr>
<tr>
<td>4600x70, Ni 4%, 90 min, 1.0 mm</td>
<td>3.35</td>
<td>3.33</td>
<td>0.67</td>
</tr>
<tr>
<td>3600x70, Ni 2%, 90 min, 0.5 mm</td>
<td>3.32</td>
<td>3.32</td>
<td>0.10</td>
</tr>
<tr>
<td>4600x70, Ni 2%, 90 min, 1.0 mm*</td>
<td>4.83</td>
<td>4.83</td>
<td>0.15</td>
</tr>
</tbody>
</table>

* Higher heating rate
Figure 2-1. Schematic diagram of Theta Composer
Figure 2-2. Schematic diagram of hydrogenation system
Figure 2-3. Surface morphology change (Rotor speed: 4600 rpm, Gap Size: 1 mm, Mg-2 wt % Ni): (a) Pure 44 μm Mg particle, (b) 44 μm Mg-2 wt % Ni particle (After dry coating, Before Hydrogenation)
Figure 2-4. Distribution of Ni nano particles on Mg (Rotor speed: 4600 rpm, Gap Size: 1 mm, Mg-2 wt % Ni): (a) SEM, (b) EDS mapping of Ni
Figure 2-5. Particle texture change (Rotor speed: 4600 rpm, Gap Size: 1 mm, Mg-2 wt % Ni); (a) Pure 44 μm Mg only, (b) after hydrogenation (Initial hydrogen pressure: 145 psi, Hydrogenation time: 300 min, Temperature: 483K)
Figure 2-6. XRD patterns for MgH$_2$ -2 wt % Ni Composites (Initial hydrogen pressure: 145 psi, Hydrogenation time: 300 min, Temperature: 483K)
Figure 2-7. Effect of coating time on H<sub>2</sub> absorption (Rotor speed: 4600 rpm, Gap Size: 1 mm, Mg-2 wt % Ni, Initial hydrogen pressure: 145 psi, Hydrogenation time: 300 min, Temperature: 483K)
Figure 2-8. Profile for hydrogenation runs with material Mg-2 wt % Ni (90 min): (a) Rotor speed: 3600 rpm, (b) Rotor speed: 4600 rpm (Initial hydrogen pressure: 145 psi, Hydrogenation time: 300 min, Temperature: 483K)
Figure 2-9. Effect of Ni loading & gap size on H₂ absorption: (a) Effect of Ni loading (Rotor speed: 4600 rpm, Gap Size: 1 mm, Coating time: 90 min), (b) Effect of gap size (Rotor speed: 3600 rpm, Ni wt %: 2 %, Coating time: 90 min) Hydrogenation condition (Initial hydrogen pressure: 145 psi, Hydrogenation time: 300 min, Temperature: 483K)
Figure 2-10. Effect of heating rate on H₂ absorption (Rotor speed: 4600 rpm, Ni wt %: 2 %, Coating time: 90 min, Gap size: 1 mm)
Figure 2-11. Hydrogen desorption analysis by TGA
CHAPTER 3
MODEL FOR HYDROGEN ABSORPTION KINETIS AND CAPACITY IN METAL HYDRIDIES

Introduction

Over the past decade, the use of hydrogen as an alternative fuel has been of particular interest to many applications, from mobile electronics to aerospace industries (DOE 2007a; NASA 2006; Schlapbach and Züttel 2001). Among various available methods for hydrogen storage, solid storage using reversible metal hydrides is considered to be one of the most promising (Biswas and Wu 2005; Schlapbach and Züttel 2001). The advantages of reversible metal hydrides include improved safety, environmental friendliness, and a relatively high hydrogen storage capacity. One main limiting factor, however, is the high temperature required for the formation of metal hydrides with acceptable hydrogen uptake and release kinetics, which makes them expensive processes (Fukai 2005; Schlapbach and Züttel 2001).

There have been many experimental studies in recent years to understand the rate-limiting kinetics and absorption capacity of hydrogen storage in alloys (Fukai 2005; Holtz and Imam 1999; Liang et al. 1998; Liang et al. 1999; Orimo and Fujii 1996; Yang et al. 2000). Holtz and Imam (1999) proposed that nucleation of metal hydride on the surface of pure metal is the initial rate limiting step for absorption of hydrogen, as initial hydrogenation (i.e. nucleation of metal hydride) takes place only at the metal’s active surface. As hydrogenation progresses, the hydride layer (impermeable to hydrogen) thickens and expands from the surface. Diffusion through the metal hydride layer is many orders of magnitude slower than other mechanisms (i.e. nucleation of metal hydride and dissociation of a hydrogen molecule into two hydrogen atoms) and subsequently becomes the rate-limiting step in the hydrogenation process (Bloch and Mintz 1997; Friedlmeier and Groll 1997; Sastri et al. 1998; Schweppe et al. 1997).
Several empirical or theoretical kinetic models have also been formulated and subsequently fitted with experimental data for describing hydrogen absorption/desorption behavior of metal hydrides (Chou et al. 2005; Friedlmeier and Groll 1997; Ginstling and Brounshtein 1950; Rudman 1979; Saetre 2006). The nucleation and growth model developed by Avrami (Avrami 1939; Avrami 1940; Avrami 1941) is a frequently applied model for describing phase change in solids. In Avrami’s model, random nucleation and the subsequent three-dimensional growth of a new phase within the bulk is the rate-limiting step. Rudman (1979) extended Avrami’s model to metal–hydrogen systems; the effects of temperature and hydrogen pressure on the kinetics for hydrogen diffusion limited cases were considered, assuming a constant growth rate of magnesium hydride.

The other commonly accepted model for metal hydride formation was proposed by Flanagan (1978). Hydrogen molecules are adsorbed or weakly chemisorbed on an active metal surface where they dissociate into hydrogen atoms. These atoms can easily diffuse between the grain boundaries of the pure metal and then finally form metal hydride (Flanagan 1978; von Zeppelin et al. 2002). If diffusion of hydrogen atoms occurs at a fast rate along the grain boundary (i.e. the grain size is small), a metal hydride layer is formed and thickens into a pure metal core (Zaluska et al. 1999). This can be best described by “the shrinking-core model” (Levenspiel 1999). Several numerical studies have been conducted based on the shrinking-core model, considering changes in growth rate for a diffusion limited case (Chou et al. 2005; Ginstling and Brounshtein 1950; Rudman 1979; Saetre 2006; Schweppe et al. 1997).

Barkhordarian et al. (2006) reported that their experimental data of the absorption behavior of magnesium catalyzed with Nb2O₅ were better described by a three-dimensional diffusion controlled shrinking-core model. Gabis et al. (2005) also compared Avrami’s model and
the shrinking-core model with thermal desorption spectrometry (TDS) experiments of metal hydride, and the results showed that the shrinking core model better described the kinetics of hydrogen desorption. Nevertheless, predictions by both models deviate from experimental observations, especially during the initial period of the hydrogenation process (Schweppe et al. 1997; Stander 1977). The reason for the deviation stems from the key assumptions of these models that the process is diffusion limited and that the change in rate limiting mechanisms during the process is not considered. Stander (1977) divided the kinetics of Mg hydride formation into two mechanisms (nucleation and diffusion) and likewise fitted his experimental data separately for each of these cases as a function of the fraction ($\alpha$) of metal hydride. He reported that the nucleation equation was valid for pure Mg for an upper limit of 0.18 for $\alpha$. This is equivalent to a layer of 1.6 µm MgH$_2$ on a Mg particle diameter of 25 µm. After the magnesium surface was utilized ($\alpha > 0.18$), a separate equation for diffusion was reported to reproduce experimental data well.

The objectives of this chapter were to investigate the kinetics of hydrogen absorption mechanism of a metal hydride system by considering multiple mechanisms in the process. A kinetic model inclusive of interfacial and diffusion controlled growth mechanisms was developed to determine the absorption rate and capacity for isothermal conditions. The model predictions were validated by experimental data of Mg-Ni systems to demonstrate its applicability.

**Model Development**

The mathematical model developed in this study adopted the concept of a shrinking-core spherical particle described in previous literature (Levenspiel 1999). Figure 3-1 shows the conceptual schematic of the shrinking core with three sequential steps for hydrogenation considered in this study:
**Step1**: Dissociation of hydrogen molecules into hydrogen atoms at the interface of the catalyst and the Mg particle surface.

**Step2**: Diffusion of hydrogen atoms through the surface layer of MgH₂ and into the volume of the unreacted Mg core.

**Step3**: Interfacial growth of hydride.

An issue that requires attention is that the true value of hydrogen atom concentration cannot be measured in our system. Furthermore, the system can not distinguish between interfacial growth and dissociation. To circumvent this problem, it was assumed that dissociation of hydrogen molecules into atoms at the interface was instantaneous. Therefore, the equivalent molar concentration of hydrogen atoms ($C_H$) chemisorbed is twice the molar concentration of hydrogen molecules ($C_\text{H}_2$) in gas. As a result, dissociation is overlooked and only two steps are considered in our model: diffusion of the hydrogen atoms, and interfacial growth with the Mg core to form MgH₂. The following sections describe the development of the model for isothermal conditions.

**Absorption Kinetics**

**Diffusion**

The rate of diffusion of H can be expressed as the flux across the area of unreacted core with the concentration gradient as the driving force as follows.

$$-\frac{dN_H}{dt} = 4\pi r^2 D \frac{d(C_H(t) - C_d)}{dr}$$

(3-1)
where $C_H(t)$ is the concentration of hydrogen atom chemisorbed in MgH$_2$ at time, $t$. This applies to an experimental situation where hydrogen pressure in the chamber and hence $C_H(t)$ decreases with time $t$. $C_d$ is the maximum solubility of hydrogen atoms in magnesium (Callister 1997; Ovrelid et al. 1998; Ragone 1995; Zeng et al. 1999). Compared to the hydrogen concentration in a typical hydrogenation chamber (approximately 30 ppm at 300 °C at 1.5 Mpa of H$_2$ atmosphere) (Ovrelid et al. 1998), $C_d$ is very small and is therefore neglected. The definition of each variable is given in the Nomenclature section.

Interfacial Growth

Assuming that the growth of MgH$_2$ is interfacial controlled, the rate of MgH$_2$ formation can be considered as a first ordered reaction and hence proportional to the hydrogen atom concentration and the available interface area of unreacted Mg. Therefore, the loss of H per unit time due to interfacial growth can be expressed as:

$$-\frac{dN_H}{dt} = 4\pi r_c^2 k''C_H(t)$$

(3-2)

Overall Process

The consumption of two H atoms due to growth of MgH$_2$ requires one Mg atom, i.e.

$$dN_{Mg} = \frac{1}{2} dN_H$$

(3-3)

The change of number of Mg atoms can then be related to the change of Mg core volume and its shrinking radius as

$$dN_{Mg} = \rho_{Mg} dV_c = \rho_{Mg} \frac{4}{3} \pi r_c^3 = \rho_{Mg} 4\pi r_c^2 dr_c$$

(3-4)

In this calculation, the volume and density change due to the formation of MgH$_2$ is ignored.

Incorporating these equations (3-1 ~ 3-4) gives the following overall MgH$_2$ formation rate in terms of the change in Mg particle radius.
Solution to Rate Limiting Condition

The solution to the kinetic equation can be obtained by considering the initial condition and mass balance. The initial condition (for an isothermal system) is:

\[ t = 0, r_c = R \]  \hspace{1cm} (3-6)

The variation of H₂ concentration in the gas phase with time can be related to the change of core diameter using a simple mass balance expression,

\[ C_{H₂}^0 - C_{H₂}(t) = \rho_{Mg} \frac{4\pi N}{3V} (R^3 - r_c^3(t)) \]  \hspace{1cm} (3-7)

The results for each rate limiting case are discussed below.

Interfacial Growth Limited Case

When the process is interfacial growth-limited, Equation 3-5 in a system with varying H₂ concentration (Equation 3-7) can be simplified as

\[ \frac{1}{(Mr_c^3 + Q)\frac{dr_c}{dt}} = -\frac{k''}{\rho_{Mg}} \]  \hspace{1cm} (3-8)

where \( M = \rho_{Mg} \frac{4\pi N}{3V} \) and \( Q = [C_{H₂}^0 - MR^3] \)

Using Equation 3-6, the solution can be obtained as

\[ \frac{1}{6} \frac{\rho_{Mg}}{k''Ma^2} [2(f - g) + (e - d) + (c - b)] = -t \]  \hspace{1cm} (3-9)

where “a” through “g” are expanded as follows:
\[
a = \left(\frac{O}{M} \right)^{1/3}
\]
\[
b = 2\sqrt{3} \tan^{-1} \left( \frac{1}{\sqrt{3}} \left( \frac{-2r_c(t) + a}{a} \right) \right)
\]
\[
c = 2\sqrt{3} \tan^{-1} \left( \frac{1}{\sqrt{3}} \left( \frac{-2R + a}{a} \right) \right)
\]
\[
d = \ln(r_c^2(t) - r_c(t)a + a^2)
\]
\[
e = \ln(R^3 - Ra + a^2)
\]
\[
f = \ln(r_c(t) + a)
\]
\[
g = \ln(R + a)
\]

Diffusion Limited Case

As the hydride layer grows thicker, diffusion through the layer becomes a stronger barrier that controls the rate. Equation 3-5 can then be reduced to the following

\[
- \frac{dr_c}{dt} = \frac{DR}{\rho_{Mg} (R - r_c) r_c} \left[ C_{H_2}^0 - M \left( R^3 - r_c^3 \right) \right]
\]  \hspace{1cm} (3-10)

Using the same initial condition (Equation 3-6), the solution can be obtained as

\[
\frac{1}{6} \frac{\rho_{Mg}}{D M a R} \left[ 2(f - g)R - (d - e)R + (b - c) + 2a(h - i) \right] = t
\]  \hspace{1cm} (3-11)

where “h” and “i” are expanded as follows:

\[
h = \ln(Q + Mr_c^3(t))
\]
\[
i = \ln(Q + MR^3)
\]

Comparisons with Equations Reported in the Literature (constant C_{H_2})

For a constant hydrogen concentration, the solution to Equation 3-10 can be obtained as

\[
\frac{2r_c^3}{3} - Rr_c^2 + \frac{R^3}{3} = \frac{2RDC_{H_2}t}{\rho_{Mg}}
\]  \hspace{1cm} (3-12)
Equation 3-12 can be further transformed using the following relationship between $r_c$, $\alpha$ and $R$

$$\frac{r_c}{R} = (1 - \alpha)^{\frac{1}{3}} \quad (3-13)$$

The resultant equation is

$$1 - \left(\frac{2\alpha}{3}\right) - (1 - \alpha)^{2/3} = \frac{2}{R^2\rho_{Mg}}C_{H2}Dt \quad (3-14)$$

This is identical to the shrinking core model with three-dimensional diffusion (Ginstling and Brounshtein 1950) as expressed by:

$$1 - \left(\frac{2\alpha}{3}\right) - (1 - \alpha)^{2/3} = Kt \quad (3-15)$$

where $K$ was called the overall coefficient as shown in earlier studies (Ginstling and Brounshtein 1950). Indeed, $K$ is a function of particle size, hydrogen pressure, and the diffusion coefficient of hydrogen.

Overall Equation with Two Mechanisms

Equation 3-5 coupled with Equation 3-7 yields an equation that includes two mechanisms for a varying hydrogen concentration

$$-\frac{dr_c}{dt} = \frac{Q + Mr^3_c(t)}{\rho_{Mg}} - \frac{\rho_{Mg}}{(R - r_c)r_c} + \frac{1}{RD} + \frac{1}{k''} \quad (3-16)$$

The solution to Equation 3-16 is
While Equation 3-15 provides a simple form, its applicability is limited to the assumptions of constant hydrogen concentration and a “diffusion only” case. Equation 3-17 allows comparison of various rate limiting steps and hydrogen concentrations. Such comparisons have not yet been systematically reported for the entire hydrogenation process.

**Experimental**

**Characterization of Hydrogen Absorption Kinetics**

Mg particles coated with nano Ni catalyst were prepared using a dry coating system (Theta Composer, Tokuju Corp.). Hydrogen absorption was studied using a custom-made hydrogenation system, which is shown in Figure 3-2. The methodology used in sample preparation and the elements of the hydrogenation system have been described in depth elsewhere (Jeon et al. 2006). Only the experimental conditions used in this study are outlined here. 0.907 g of Mg-Ni composite was used in the experiment and was prepared under a controlled argon environment in the glove box. The hydrogenation chamber was heated using heating tapes (Omega FGS101-040, 420 W) while in vacuum. After the chamber reached the designed temperature (463, 483, 503, and 523 K), pure hydrogen of targeted pressure (0.5, 1.0, and 2.0 MPa) was then immediately introduced. The temperatures inside and outside of the chamber were controlled using a DAQ (data acquisition module, Omega DAQ-55). Internal temperature and chamber pressure data were recorded automatically.

\[
\frac{1}{6k''Ma^2} \{2(f-g) + (e-d) + (c-b)\} DR \\
- 2(f-g) + (e-d) - (c-b)k''aR \\
- 2(h-i)k''a^2 = -t 
\]  

(3-17)
Transmission Electron Microscopy

Dual focused ion beam milling technique (FEI DB 235) with a gallium liquid metal ion source (LMIS) was used to prepare thin foil for transmission electron microscopy (TEM). This technique was successfully employed to prepare a 100 nm thick sample from a 44 μm Mg-Ni composites hydrogenated under 1 MPa of hydrogen at 483K. The sample was imaged in the FIB system using a 5 KV beam to minimize possible damage to hydride structure. A thin layer of platinum was deposited on the surface via an in situ needle platinum aspirator that was positioned 80 mm above the region of interest. Micrographs and diffraction patterns of the sample were analyzed in JEOL TEM 200CX.

Presence of MgH₂ Layer near Surface

Several experimental studies have been conducted to explain hydrogen absorption behavior of metals (Friedlmeier and Groll 1997; Fukai 2005; Gabis et al. 2005; Jeon et al. 2006; Liang et al. 1998; Liang et al. 1999; Orimo and Fujii 1996; Stander 1977; von Zeppelin et al. 2002; Yang et al. 2000; Zaluska et al. 1999). However, these studies did not identify the actual mechanisms of MgH₂ formation in Mg particles and there is a need for clarity (Bloch and Mintz 1997). Figure 3-3(a) shows the formation of the hydrogenated layer (Region A) near the surface of the Mg-Ni composite particle. The partial cracks observed on the same layer shown in Figure 3(b) are an indication of volume expansion when MgH₂ formed. Similar observations of volume expansion have been reported in prior Mg hydride studies (Bloch and Mintz 1997; Friedrichs et al. 2007).

The hydrogenated layer thickness varied considerably, suggesting that the interfacial controlled growth mechanism of hydride is a valid assumption. When the growth is solely diffusion controlled, this layer is anticipated to have a constant thickness. The maximum depth of the reacted layer measured graphically in Figure 3-3(a) is 4.2 μm which is capable to the
theoretical average thickness of 5.2 μm based on the observed hydrogen capacity of 4.2 wt. %. The difference between the two values likely comes from the assumptions of sphericity and smooth surface in the equation.

Figures 3-3 (c) and (d) show the electron diffraction patterns (DP) of areas (A) and (B) marked in Figure 3-3(a). For identical magnification and SAD aperture size, area (B) exhibited a single crystal DP while highly dense ring DP from area (A) demonstrates that this area consists of ultra-fine magnesium grains. The DP from the latter area also showed the presence of MgO, which was possibly formed during sample preparation. Although the XRD profile of the hydrogenated material showed the formation of MgH₂ phase (Jeon et al. 2006), the TEM sample did not reveal the presence of this phase. Similar observation has been made other studies (Friedrichs et al. 2007; Friedrichs et al. 2006; Shao et al. 2004).

When MgH₂ is exposed to the electron beams under TEM with a high vacuum condition, the release of hydrogen gas commences within a few seconds (Friedrichs et al. 2007; Friedrichs et al. 2006; Shao et al. 2004) and dehydrogenated MgH₂ results in the formation of very fine Mg crystals (Schober 1981). Therefore, the above results indicate that area (A) had been the MgH₂ layer, which was converted to ultra-fine grained Mg during the imaging process or possibly sample preparation.

**Determination of Diffusion and Interfacial Growth Coefficients for Hydrogenation**

A limited number of hydrogen diffusion coefficients in MgH₂ have been reported in previous studies (Bowman and Fultz 2002; Cui et al. 2001; Nishimura et al. 1999). However, the values of diffusion coefficients obtained from these studies vary significantly (6 orders of magnitude). One possible reason for this can be the differences in grain sizes of sample in these experiments, although such information is not available. Several researchers (Callister 1997; Higuchi et al. 1999; Revesz et al.; Varin et al. 2006; Zaluska et al. 1999) have performed hydrogen
diffusion/nucleation experiments using single- and poly-crystals with controlled grain size. Results showed that reduced grain size of the metal powder enhances diffusion of hydrogen atoms within the metal, leading to increased metal hydride formation. It should also be noted that the concept of interfacial controlled growth of hydride has not been suggested prior to this study.

Figure 3-4 shows the change in hydrogen pressure as a function of hydrogenation time in a typical experiment using the hydrogenation system. In this study, based upon the proposed analytical model, the absorption curve is divided into four regimes (i.e., incubation, interfacial growth limited, transition, and diffusion limited). The interfacial growth coefficient (k") was obtained from the change of hydrogen pressure in the interfacial growth limited regime (Region b in Figure 3-4) using Equation 3-9. For the diffusion coefficient (D), the change of hydrogen flux was used to interpret the relationship using Equation 3-11, which is applicable in the diffusion-limited regime of the hydrogenation process (Figure 3-4D).

Figure 3-5 shows hydrogen diffusion and interfacial growth coefficients as a function of temperature with three replicated experiments for each condition. The hydrogen diffusion activation energy (Ea) of the Mg-2 wt. % Ni composites was calculated using an Arrhenius form, as shown in Figure 3-5(a). The activation energy was found to be 2.38 Kcal/mol, which is significantly lower than that of the bulk magnesium measured by Nishimura (1999), which was 24.1Kcal/mol. Activation energy of interfacial growth coefficient was 9.28 Kcal/mol. The activation energy of hydrogen diffusion did not demonstrate temperature effect on diffusion coefficient adequately. It is to be noted that experimental results are valid within the range of temperatures studied. Other fundamental assumptions that were made are listed as follows.

- Mono-disperse spherical Mg particle of diameter 44 µm
Hydrogen atom concentration chemisorbed on MgH₂ is half of hydrogen molecule concentration the gas phase (i.e., activation energy for vacancy formation in MgH₂ was neglected).

**Comparative Study of Experimental and Calculated Data**

Using the diffusion and interfacial growth coefficients obtained, hydrogen absorption capacity can be determined using Equation 3-17 and was compared to the experimental value. Figure 3-6 shows the absorption behavior of Mg-2 wt. % Ni composites as a function of hydrogenation time at 483 K. The model predictions (interfacial growth and diffusion), as shown, are almost identical to the experimental data for the entire hydrogenation process. The model prediction considering diffusion only, on the other hand, shows a slower increase in the beginning. The close fit of the calculated and experimental data shown in Figure 3-6 verifies the hypothesis that there are two major rate-limiting mechanisms in the hydrogenation process: in the beginning, interfacial limited growth of metal hydride is the rate limiting mechanism which changes to diffusion upon the thickness of the hydride layer. This is depicted by the steep initial increase, followed by a gradual decrease in the rate of change of hydrogen penetration depth with increasing hydrogenation time.

**Effect of Temperature and Initial H₂ Pressure on Hydrogen Absorption Kinetics**

While the effect of temperature on hydrogen absorption capacity has been quantified within bounds of experimentation for decades (Fukai 2005; Liu et al.; Rudman 1979; Saetre 2006; Sastri et al. 1998; Schlapbach and Zuttel 2001; Song 1995; Stander 1977), the effect of temperature on hydrogen absorption kinetics has rarely been quantitatively modeled. Figure 3-7a presents the effects of temperature on hydrogen absorption predicted by the model. Experimental data obtained for 3 temperatures at 4 hydrogenation times are also displayed. The results for the Mg-2 wt. % Ni composites tested shows linear trends for the same hydriding time within the
The dependence of hydrogen absorption on initial hydrogen pressure was also evaluated. Initial hydrogen pressure was varied from 0.5 and to 2.0 MPa. Figure 3-7b shows the hydrogen absorption capacities plotted as a function of initial hydrogen pressure. Both the model prediction following Equation 3-17 and the experimental data are presented. As shown, the model can provide a holistic picture of expected behavior based on broad assumptions to closely simulate practical situations.

**Effect of Mg Particle Diameter on Hydrogen Absorption Kinetics**

The diameter of magnesium particles has been identified as an important variable from experimental studies for metal hydrides (Varin et al. 2006; von Zeppelin et al. 2002; Yang et al. 2000; Zaluska et al. 1999). In practical applications, hydrogen refueling time at a station is one of the key technical barriers for usability of metal hydrides (DOE 2007a; DOE 2007b; Schlapbach and Zuttel 2001). DOE’s technical targets of refueling time for a storage system are on the order of 5 minutes or less by 2007 and 3 minutes by 2012 (DOE 2007b). In this study, the model was used to determine hydrogenation time required to reach the theoretical hydrogen absorption capacity of Mg ($\tau$) as a function of particle diameter. Simulation runs were performed for particle size from 1.25 $\mu$m to 44 $\mu$m with all the other parameters kept the same. Figure 3-8a shows the results of hydrogen absorption capacity as a function of hydrogenation time for 5 magnesium diameters. The samples composed of smaller Mg particles tend to have thinner MgH$_2$ layers and achieve the target hydrogen capacity much faster than their larger counterparts. In other words, smaller particles are interfacial growth limited while larger particles experience diffusion limited conditions (as exhibited by their slope). Figure 3-8b shows hydrogenation time as a function of magnesium particle diameter. It can be seen that the hydrogen refueling time, of
great interest to practical application, can be drastically reduced to meet the DOE criteria for the hydrogen refueling time by changing the diameter of Mg particle. To meet the DOE criteria set for 2012, the particle size of the Mg-2 wt% Ni used in this study should be 1.25 μm (τ = 2.7 min) or smaller. Nevertheless, a larger particle size can be used under higher pressure or temperature, as discussed in the previous section.

Summary

The kinetics of formation of magnesium hydride layer on Mg-Ni composites was studied. It was verified by SEM/TEM characterization that magnesium hydride layer formed from the surface rather than from random interfacial growth and growth in Mg. The formation of the hydride layer verifies that in the beginning of hydrogenation process, interfacial growth of MgH₂ is the rate limiting mechanism and as time goes on, diffusion of hydrogen through the MgH₂ layer becomes the rate limiting mechanism. This observation provides an insight into the partitioning of the rate limiting mechanism between interfacial growth and diffusion, and it forms the basis for the analytical model.

The analytical model was developed for evaluating the change of rate-limiting mechanisms of Mg-Ni composites with regards to hydrogen absorption rate and capacity, taking hydrogenation kinetics as a function of hydrogenation time into account. The agreement between modeled and experimentally measured data was excellent. The model reproduced the change in the rate limiting mechanism of hydrogenation from interfacial growth of metal hydride to diffusion through the hydride layer into the Mg particle core. The activation energy of diffusion coefficient (2.38 Kcal/mol) of the Mg-2 wt. % Ni composites was found to be significantly lower than that of pure Mg (24.1Kcal/mol). Activation energy of MgH₂ interfacial growth coefficient, which has never been reported before, was 9.28 Kcal/mol.
The hydrogen absorption capacity can be predicted as a function of the temperature, hydrogen pressure and Mg particle diameter at the given hydrogenation time. The time needed to hydride a Mg particle drastically decreases as its size decreases, and it decreases as temperature and pressure increase. As demonstrated, the new model developed in this study can more accurately describe hydrogen absorption capacity and kinetics, as it accounts for the effects of all important parameters: interfacial growth of metal hydride, diffusion of hydrogen and a variable hydrogen concentration.

**Nomenclature**

- $C^0_{H_2}$: Initial Concentration of $H_2$ in gas phase [mole/m$^3$]
- $C_{H_2}$: Concentration of $H_2$ in gas phase [mole/m$^3$]
- $C_H$: Concentration of $H$ in MgH$_2$ [mole/m$^3$]
- $C_d$: Concentration of $H$ dissolved in Mg [mole/m$^3$]
- $D$: Diffusion coefficient [m$^2$/s]
- $d_p$: Particle diameter [m]
- $k$: Hydrogen dissociation constant [m/s]
- $k''$: Interfacial growth coefficient [m/s]
- $K$: Overall coefficient in shrink core model [1/s]
- $N$: Number of Mg particles in the sample [-]
- $N_{H_2}$: Moles of hydrogen molecule in gas phase [mole]
- $N_H$: Moles of hydrogen atom in solid phase in the system [mole]
- $N_{Mg}$: Moles of Mg particle [mole]
- $r_c$: Radius of Mg particle as a function of time [m]
- $R$: Initial Mg particle radius [m]
- $R_{gas}$: Ideal gas constant [cal/K.mol]
- $T$: Temperature [K]
- $t$: Time [sec]
- $V$: Volume of hydrogenation chamber [m$^3$]

**Greeks**

- $\alpha$: Metal hydride volume fraction [-]
- $\theta$: Fraction of the catalyst coated area [-]
- $\rho_{Mg}$: Molar concentration of Mg particles in the system [mole/m$^3$]
- $\tau$: The time required to reach theoretical hydrogen absorption capacity [min]
- $v_c$: Volume of the shrinking Mg core [m$^3$]
Figure 3-1. Schematic diagram of the shrinking core model
Figure 3-2. Schematic diagram of the hydrogenation system
Figure 3-3. SEM/TEM micrographs and electron diffraction patterns obtained for the hydrogenated Mg-Ni: (a) SEM picture showing the hydrogenated layer near the surface of the Mg-Ni particle, (b) TEM micrograph showing the formation of microcracks in the hydrogenated region, (c) diffraction pattern obtained from area (A), (d) diffraction pattern obtained from area (B)
Figure 3-4. Change in hydrogen pressure as a function of time (44 μm Mg + 2 wt. % Ni, initial H₂ pressure = 1 MPa): (a) Incubation regime, (b) Interfacial growth limited regime, (c) Transient regime, and (d) Diffusion limited regime
Figure 3-5. Determination of hydrogen absorption coefficient following the Arrhenius form: a) Diffusion coefficient, b) Nucleation coefficient
Figure 3-6. Comparison of measured and model data (Simulation condition: 44μm Mg + 2 wt. % Ni, initial H\textsubscript{2} pressure = 1 MPa, temperature = 483 K): (a) Incubation regime, (b) Interfacial growth limited regime, (c) Transient regime, and (d) Diffusion limited regime.
Figure 3-7. Effect of temperature and initial hydrogen pressure on hydrogenation: (a) effect of temperature (initial pressure = 1.0 MPa), (b) effect of initial hydrogen pressure (Temperature: 483 K)
Figure 3-8. Effect of Mg particle size on hydrogen absorption kinetics (simulation condition: Mg + 2 wt. % Ni, initial H₂ pressure = 1.0 MPa, temperature = 483 K); (a) Hydrogen absorption capacity as a function of hydrogenation time for various Mg particle sizes, (b) effect of magnesium particle size on τ.
CHAPTER 4
FLAKE PARTICLE SYNTHESIS FROM DUCTILE METAL PARTICLES USING A NOVEL HIGH-SPEED VIBRATORY MILL

Background

A flake-shaped particle is a particle with a high diameter-to-thickness aspect ratio. Needs for flake particles vary across a variety of applications such as: pigments and inks, electrochemical electrodes, fuel cell hydrogen storage devices, explosives, lightweight concretes and obscurances (Cashdollar 2000; Hong and Kim 2001; Hong et al. 2000; Lee et al. 2002; Trunov et al. 2005; Yoshinaga et al. 2002). Properties of flake-shaped particles have growing interests in the chemical and material industries, which continuously demand for increased efficiency in their processes. Flake particles are desirable from several viewpoints. Due to its high aspect ratio, a flake particle has a larger specific surface area than a spherical particle of the same volume, which can enhance chemical reactivity (Cashdollar 2000; Trunov et al. 2005). High aspect ratio metal flakes, such as those made of aluminum, have been used to increase optical obscurance characteristics so as to mimic a metallic look when used as pigment in paint (Smith et al. 2003). Additionally, the use of flake powders for metal-hydride electrodes in modern batteries has shown significant improvement in electrical capacity (Yoshinaga et al. 2002; Yoshinaga et al. 1997). Processes for the production of flake-shaped particles are relatively new and have yet to be extensively studied and mastered. Conventional methods for flake particle synthesis are Attritor milling, vibratory ball milling, ball milling and wet milling (Hong and Kim 2001; Hong et al. 2000; Kilinc et al. 2004).

Attritor mills generally refer to the use of a stirring rod and pin to agitate a solution of grinding media and the target particles. During such agitation, the random collisions of balls statistically occur with the target particle in between, eventually flattening the particle after successive impactions (Kilinc et al. 2004). This method, however, can take at least 5 hours to
produce consistent flake particles, wasting a large amount of energy to fluid friction and fruitless collisions, and also requires milling to occur in a liquid solution, which can react with the target particle (Kilinc et al. 2004). A vibratory mill operates under similar circumstances as that of the previously mentioned attritor mill; however, it produces a high frequency of randomly colliding ball media by the means of large vibrating forces, and it does not require a liquid milling solution (Dunlap et al. 2000). Though this method allows for the highest kinetic transfer of those mentioned, it is also bounded by long operating times (up to 8 hours; e.g. SPEX model 8000)(Dunlap et al. 2000). Ball milling methods typically require lubricants and anticoagulants such as stearic or oleic acid and/or mineral spirits to control the shape and quality of the product flake (Hong and Kim 2001; Hong et al. 2000). These reagents are incompatible when reactive metals such as Al, Fe, Mg, and Cu must remain in their elemental form and can possibly react with the reagents during milling, especially when high energy transfers are present. Wet milling methods such as basket mills are not compatible for similar reasons. Furthermore, these conventional methods are very time-consuming, ranging in processing time from 0.5 to 60 hours (Hong and Kim 2001; Hong et al. 2000; Kilinc et al. 2004; Lee et al. 2002; Yoshinaga et al. 1997). As an example, Hong and Kim (2001) reported that processing scrap aluminum particles in a wet ball mill system with oleic acid requires 30 hours to produce flake particles of micrometer thickness.

The objective of this chapter was to develop a novel high-speed vibratory mill process for the production of flake particles so as to significantly reduce the milling time required to achieve micrometer thickness without the need of subsidiary milling aides. During milling operations, a cycle of particle fragmentation and reformation was observed. The effects of plastic deformation, particle-to-particle welding and flake fragmentation of this cycle on particle size distribution
were examined. Several operating parameters of the milling process were studied, including milling time, particle medium (i.e. Fe, Mg), initial particle size, loading weight and ball media size.

**Mechanisms**

**High Speed Orbiting of Ball Media**

The milling operation occurs within a closed milling tube, where spherical particles are subjected to strong compression and shear forces produced by ball media that flatten the particles. The motion of ball media in the milling tube is illustrated in Figure 4-1 (a). Compression and shear forces are produced by ball media that roll along the smooth inner wall of the milling tube at high speeds (several thousand rotations per minute) forming sustained orbiting regions. Figure 4-1 (b) is a photograph demonstrating the orbits created by the rolling ball media that are visible as long circular blurs functioning inside a glass test-tube.

Oscillations in the xz-plane of the milling tube produce the impetus for the media motion. Figure 4-2 illustrates the frame-by-frame movements of the milling tube and the resulting movement of the containing media. The motion of the milling tube is indicated as going in the direction from the gray position to the black position. The oscillations of the milling tube from position 1 → 2 → 3 → 4 repeated, cause an acceleration with a continuously changing direction away from the milling tube center – indicated as a gray arrow. In turn this causes the internal ball media to naturally find the opposite-most point from the direction of milling tube movement. This point is indicated by the position of the dark and filled ball media in Figure 4-2. With a continuous change in the direction of the milling tube acceleration, the position of the ball media likewise changes continuously. Ultimately this motion causes the internal media to roll along the inside edges of the milling tube at the same frequency as the milling tube oscillation.
Plastic Deformation and Welding Effects

In the context of the presented novel milling system, plastic deformations are shape changes occurring to the initial particle sample during milling due to the high compression and shear forces from the orbiting ball media. Deformation occurs primarily in a way that results in very thin and wide flakes. Furthermore, progressive deformation can lead to fragmentation of flake particles, resulting in many smaller flakes. Evidence of this can be seen as an increase in the fraction of smaller particles.

Due to the high frequency of orbiting media and chaotic swirling motion of particles inside the milling tube, random flake overlaps readily occur. Composite welding occurs as various flakes are joined to one another by random overlappings resulting in a single compound flake. Instances of compound flake-to-flake welding have been reported for various types of milling devices (Huang et al. 1995; Kilinc et al. 2004; Smith et al. 2003; Yoshinaga et al. 2002; Yoshinaga et al. 1997). Since there are both large and very small particles accumulating, the resulting compound flake may be large or not so large, leading to a wider distribution of sizes for welding dominant systems. However, a compound flake must always be greater in size than its constituents, resulting in a shift of the particle size distribution towards larger particle size ranges.

Experimental

Experimental System

For this research, a lab scale version of the novel vibratory mill process was built. A milling tube was constructed using 10 mm internal diameter aluminum tubing with a length of 50 mm. Milling tubes were mounted via plastic collars perpendicular to a high-speed vibrator, which provided 13,000 oscillations per minute (OPM) at 120 V. Chromium-Steel Cr-52100 balls (Norstone Inc.) with diameters of 2.0, 4.0, and 6.0 mm were used as ball media in the milling
tube. The area between the first orbiting ball and the last orbiting ball is defined as the milling zone. Whereas, the actual area which will receive the milling forces is defined as the milling area and is the sum of the ball diameter projections on the milling tube, disregarding the inter-orbit gaps, which are considered ineffectual. This method of classification is illustrated in Figure 4-3. The milling area was fixed as being equal to a total of 12 mm for all the balls in the milling tube - such that the number of balls in each tube would be 2, 3 and 6 for the 6.0 mm, 4.0 mm and 2.0 mm sizes, respectively. This arrangement was chosen with the aim in mind to make the effective milling area approximately equal for all samples so as to replicate the effective milling area for all ball sizes. Two types of particles were tested: 300 µm magnesium (Alfa Aesar) and 140 µm iron (Fisher Sci.). Each milling tube was sealed under ambient atmosphere with plastic end caps to contain the ball media and particles. Particles were weighed and loaded into each milling tube with the ball media in the tube. After processing, the products were separated from the ball media and then stored in labeled vials for analysis. Table 4-1 displays the parameters tested for each sample.

Product Characterization

Three basic characteristics of the resulting flake particles were analyzed, including mean particle diameter, mean particle thickness and morphology. Flake particle samples were evenly distributed on glass substrates and observed under an optical microscope (Olympus BX-60) using Spot Advanced (Diagnostic Instrument, INC) image capture software to acquire sample images. The sample images were then processed with Image Pro Plus (Media Cybernetic, L.P) to calculate particle number and dimensional statistics for each sample photo batch. Martin diameter, which is defined as the length of the line parallel to a given axis that divides the particle into two equal area regions, was measured. Approximately 4000 particles were analyzed per sample. To determine the thicknesses, flake particles were suspended and solidified in an
epoxy resin. The dried epoxy was then cut transversally to obtain cross sectional slices of flakes suspended in the epoxy and subsequently examined under optical microscopy. Optical microscopy was also used to study the surface morphology of bare flake particles for evidence of increased surface cracks and multiple-flake layering from flake-to-flake welding.

Because of the nature of the milling process, and provided the understanding that the size distribution of particles is dependant on the fragmentation and welding qualities of the milling parameters, its distribution does not necessarily resemble a Gaussian curve. In this study, mean particle size and standard deviation were evaluated side-by-side, which can effectively signify in what regime (fragmentation/welding dominant) the sample distribution reflects.

**Results and Discussions**

**300 µm Mg Particle**

The original particle size distributions for 300 µm Mg are displayed in Figure 4-4 (a). The effects of increased milling time on particle size distribution (Martin diameter) and thickness of 300 µm Mg particles were studied. The results for samples 1 and 2, after milling for 1 and 2 minutes respectively, are displayed in Figure 4-5 (a) and (b).

The resulting mean diameters for samples 1 and 2 were 372 and 442 µm and the standard distributions were 195 and 386 respectively. As shown in Figure 4-5 (a) and (b), the majority of the sample remains near 400 µm after both 1 and 2 minutes of milling. The peak fraction in the mean size range decreased from 1.2 in sample 1 to 0.8 in sample 2, while fractions of larger particles increased. This shows that a significant amount of the particles in the mean size range were redistributed into larger particle sizes and the size distribution became broader with increased milling time. This growth and broadening in particle size distribution can be explained by plastic deformation and particle welding as described earlier. The lack of change in the smaller particle size regime implies that the particle fragmentation was not as important as
welding, and that there does not seem to be a change in the dominant mechanisms between 1 and 2 minutes. It can therefore be concluded that, since the mean diameter is large and increasing and that the standard deviation is also broadening, plastic deformation and composite particle welding are the dominant mechanisms over particle fragmentation in these samples.

The change in flake thickness was analyzed using microscopic images of epoxy resin slices containing the flake particles. Figure 4-6 (a) displays the change in thicknesses in samples 1 and 2. With increased milling time, it can be seen that the flake thickness distribution decreases, similar to the flake diameter trend. The mean particle thickness decreased from 300 μm of unprocessed particles to approximately 35 μm after only 1 minute. Within just 2 minutes of milling, there was an even greater decrease in flake thickness, with an average flake thickness of 12 μm. Plastic deformation is responsible for this trend, since with the start of milling, flakes are continually molded thinner. It should be pointed out that due to the nature of the milling process, not all particles are milled simultaneously. During the early periods of milling, some are fully milled while others are yet to be milled. As milling time increases, the fraction of un-milled particles decreases, and the amount of milled particles arrives at the total – therefore reducing the sample discrepancy caused by the remaining un-milled particles. This explains the decrease in the flake thickness distribution in Figure 4-6 (a). In short, the fraction of the thicker and un-milled particles greatly decreases with processing time. Figures 4-6 (b) and (c) are the microscopic images of representative flake cross-sections from samples 1 and 2, respectively. The results of samples 1 and 2 demonstrate the novel high-speed vibratory milling as a very effective and efficient process for the production of flake-shaped particles.

140 μm Fe Particle

Experiments were also carried out for Fe particles. The original particle size distributions for 140 μm Fe particles are displayed in Figure 4-4 (b) and the results for samples 3 and 4 are
displayed in Figure 4-7. The resulting mean diameters for samples 3 and 4 were 238 and 241 μm and their standard deviations 63.4 and 89.4 respectively.

It can be seen from Figures 4-7 (a) and (b) that the majority of the particle size resides in the mean range of 240 μm. Similar to Figures 4-5 (a) and (b), the peak fraction decreased and larger particles developed, resulting in a wider particle size distribution. Similar to samples 1 and 2 of magnesium particles, the most possible explanation for the broadening particle size distribution is the effect of plastic deformation and particle welding – consequences of the high compression forces imposed on the flake particles inside the milling tube. In the smaller particle size range, there is little change in particle size distribution below the mean particle size. This further affirms that samples milled up to 2 minutes do not show significant signs of particle fragmentation dominance. Rather, because of the particle size distribution shift in the larger range, welding is the dominant mechanism that influences the particle size distribution in samples 3 and 4.

Comparing the results of samples 1, 2 and 3, 4 can reveal the effects of particle material. Ductility is the primary factor that determines the sample’s dimensional results. Ductile and malleable materials (ones which have a low Young’s Modulus; Mg – 45 MPa, Fe – 211 MPa) tend to have larger particle size distribution changes over time, as they are more vulnerable to the compression and shear forces present during milling.

In addition to size characteristics, surface qualities of the flake particles were observed under optical microscope. Figure 4-8 shows the acquired images of the Fe flakes. Two main characteristics of the flakes were examined: surface morphology and evidence of flake-to-flake welding events. Comparing Figures 4-8 (a) and (b), it can be seen that the surface of these iron particles became noticeably smoother with increased time.
Additionally, evidence of flake-to-flake welding can be seen (circled in both Figures 4-8 (a) and (b)). The flake pieces circled are likely to be in an intermediate phase of the entire process; a loose flake is first taken up by another and then eventually milled until the two compress into each other to the point that they are indistinguishable.

**Effect of Ball Size**

To investigate the effect of ball size on the milling operation, in regards to mean particle size and particle size distribution, two additional samples were prepared with smaller ball sizes than that of sample 2. Samples 2, 5, and 6 can be compared for the effect of the milling ball size, with all other parameters kept constant. Their particle size distributions are graphed in Figure 4-5 (c) and (d). It can be seen clearly that a simple trend exists between the resulting mean particle size and the ball media size: as the ball size is reduced, the mean particle size reduces (442, 172 and 84 μm for 6, 4 and 2 mm ball media, respectively). This trend can be explained by the larger ball sizes creating higher compression forces due to their greater mass, resulting in thinner and wider particles.

A more detailed inspection of the particle size distributions gives clues in regards to the welding and fragmentation characteristics of each sample. As mentioned earlier, fragmentation of initial flakes, by its own nature, will result in greater numbers of smaller flakes. Conversely, welding will result in generally larger flake particles, and depending on the extent and number of weldings, can have a broad range of particle sizes. It can be seen in Figure 4-5 (c) and (d) that there is a much higher fraction of smaller particles present in sample 6 (2.0 mm balls) than in sample 5 (4.0 mm balls). In other words, there is a broader midrange distribution and a lesser fraction of small particles in sample 5 (4.0 mm balls) than in sample 6 (2.0 mm balls). This indicates that smaller ball media tend to show a dominance of fragmentation over welding, while
larger ball sizes tend to have a more profound welding impact, resulting in a broader distribution of particles. This vision is also supported by the standard deviation values for samples 5 and 6. The low welding qualities of sample 6 can also be resorted to the low compression forces present in smaller media, which may not be sufficient to join two flake particles. Since fragmentation is readily present even in smaller ball sizes, all milling processes that use larger ball media have fragmentation occurrences. They differ only in their welding ability, which so far has been the most influential factor of the samples’ particle size distribution.

**Effect of Weight Loading**

The effect of weight loading of Mg in the milling tube was studied by comparing three contrasting weights. Samples 7 and 8 were prepared of 15 mg and 35 mg respectively, and were compared to the similar sample 2 of 25 mg. Their particle size distribution graphs are displayed in Figure 4-5 (e) and (f). Comparing the trends of samples 7, 2, and 8, shows the effect of increased loading weight. As the loading weight increases, the size distribution can be seen to shift from smaller to larger particles. The mean diameter data for each sample also supports this observation (55, 442 and 997 μm for 15, 25 and 35 mg, respectively). As mentioned earlier, smaller particle sizes, like those present in sample 7, imply a dominance of fragmentation and a deficit of welding instances. Since welding can only occur when particle overlapping and milling coincide, the frequency of welding is influenced by the probability of particle overlapping, which is directly related to the particle concentration. As the loading weight of the sample is increased, the concentration increases and the probability of overlapping increases as well, resulting in a greater amount of particle-to-particle welding and ultimately a shift in the particle size distribution towards a midrange size, with a typically larger standard deviation.
Summary

Several aspects of flake characteristics produced by a novel vibratory mill process were studied, including: flake diameter, thickness, and morphology as a function of processing time, ball media count and weight loading. The results of these data showed similar particle size distribution trends in samples of magnesium and iron. With increased milling time, more particles in the larger size ranges developed. This expanding distribution can be explained largely because of the effects of plastic deformation and composite particle welding. The more ductile magnesium particles tended to show faster changes in their particle size distributions, since they were more subjective to the forces that caused the shifting distribution. Flake thickness of magnesium was found to decrease as a function of time, as did the particle thickness distribution. With compression and shear forces caused by the orbiting ball media, the flake particles were continuously milled thinner, eventually to a mean thickness of 12 μm after 2 minutes of milling. Additionally, as milling proceeded, the influence of partially milled particles reduced and welding occurrences continued thus lowered the standard deviation of flake thickness with time.

The increasing weight of the milling ball media resulted in higher compression forces, and directly affected the mean particle size and its distribution based on their greater welding effects. Smaller ball media tended to show a dominance of fragmentation over welding, while larger ball sizes tended to have a more profound welding impact, resulting in a broader distribution of particles. Increasing the concentration of flake particles (weight loading) increased the probability of overlapping and therefore resulted in a greater amount of particle-to-particle welding. This led to a shift in the particle size distribution towards a midrange size, with a larger standard deviation.
In summary, a novel vibratory mill consisting of ball media orbiting at high revolutions inside a milling tube produced high compression and shear forces capable of processing 25 mg of 300 μm spherical magnesium particles into flakes of mean diameter 442 μm and thickness of 12 μm in only 2 minutes. As demonstrated, the novel high-speed vibratory mill process is a very efficient and effective process for the production of flake-shaped particles from ductile metal particles.
Table 4-1. Experimental conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle medium and size (µm)</th>
<th>Weight loading (mg)</th>
<th>Ball media count and size (mm)</th>
<th>Milling time (min)</th>
</tr>
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<tbody>
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<td>3</td>
<td>Fe, 140</td>
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</table>
Figure 4-1. (a) Schematic diagram of orbiting motion; (b) Photograph of orbiting media in glass tube (the circular blurs are trails of ball movement)
Figure 4-2. Schematic diagram of basic orbiting media mechanisms
Figure 4-3. Milling zone and milling area classification
Figure 4-4. Particle size distributions for original particles: (a) 300 µm Mg and (b) 140 µm Fe
Figure 4-5. Particle size distributions for Mg particle (300 μm): (a) sample 1, (b) sample 2, (c) sample 5, (d) sample 6, (e) sample 7, and (f) sample 8
Figure 4-6. Thickness of Mg particle as a function of milling time: (a) particle thickness distribution, (b) cross-sectional images for 300 μm Mg particle after 1 minute and (c) 2 minutes
Figure 4-7. Particle size distributions for iron particle (140 μm) as a function of milling time: (a) sample 3 and (b) sample 4
Figure 4-8. Optical microscope images at 20x magnification of iron particle: (a) sample 3 and (b) sample 4
CHAPTER 5
ENHANCED HYDROGEN ABSORPTION KINETICS FOR HYDROGEN STORAGE USING MG FLAKES FABRICATED BY A HIGH SPEED ORBITING BALL MEDIA PROCESSOR

Background

Among the various light metals and alloys that are capable of absorbing/desorbing large amounts of hydrogen, magnesium has been considered a promising candidate for solid hydrogen storage due to its high volumetric/gravimetric capacity, ease of availability and low cost (Chalk and Miller 2006; Schlapbach and Züttel 2001). The hydrogenation process starts from physisorption of hydrogen molecules onto the surface of magnesium particles, followed by dissociation into hydrogen atoms. The hydrogen atoms thus obtained diffuse into magnesium lattices to initiate nucleation and growth of magnesium hydride (Bloch and Mintz 1997; Conner and Falconer 1995; Fukai 2005). However, the major disadvantage of utilizing pure magnesium is its slow absorption of hydrogen, which is due to its low affinity for hydrogen physisorption, and the formation of a dense magnesium hydride layer (Atkins and DePaula 2002; Fukai 2005; Schlapbach and Züttel 2001). The hydride layer becomes a resistive barrier for subsequent hydrogen diffusion into the bulk and therefore results in limited material utilization. This ultimately becomes a crucial rate-limiting mechanism in the hydrogenation process (Bloch and Mintz 1997; Friedlmeier and Groll 1997; Jeon et al. 2006).

Various attempts have been undertaken to chemically improve the kinetics of Mg by incorporating transition metals such as Ni, V, Fe and Ti (Holtz and Imam 1999; Huot et al. 1999; Iwakura et al. 2002; Iwakura et al. 1999; Jeon et al. 2006; Liang et al. 1998; Varin et al. 2006; Zaluska et al. 1999). The addition of transition metals with high affinities for chemisorption results in interfacial catalysis of H₂ dissociation thus reducing the activation energy required for
dissociation of hydrogen molecules (Sandrock et al. 2002; Stillesjo et al. 1993). The resultant hydrogen atoms can more easily diffuse than hydrogen molecules along grain boundaries of magnesium (Lueking and Yang 2004; Rozanov and Krylov 1997). In addition, it has been demonstrated that the onset temperature for hydrogen absorption can be lowered by approximately 170°C by adding a small amount of Ni onto Mg (Holtz and Imam 1999). Studies report that a homogeneous distribution of nano catalysts on the metal drastically reduces the activation energy of hydrogen diffusion and results in faster formation of metal hydride even in the presence of oxides and hydroxides (Au 2005; Huot et al. 2001; Jeon et al. 2007; Seayad and Antonelli 2004; Zaluska et al. 2001). However, it should be noted that when hydrogen diffusion was the rate limiting mechanism, Ni wt. % loading showed negligible impact on H₂ absorption rate and capacity, (Jeon et al. 2006). In addition, the particle diameter of the catalyst has been also recognized as an influential parameter. Varin et al. (2006) investigated the effect of Ni particle size (micro, submicron and nano sizes) on the hydrogen absorption/desorption kinetics of 44 μm Mg powder. The addition of nano Ni was observed to greatly improve the hydrogen absorption/desorption rate as compared to micron/submicron sized catalysts.

The kinetics of hydrogen absorption and desorption of metal hydrides have also been improved mechanically by increasing the specific surface area and grain boundaries, reducing the grain size of the metal powders, and altogether enhancing diffusion of hydrogen atoms within the metal leading to increased hydride formation (Doppiu et al. 2004; Holtz and Imam 1999; Huot et al. 1995; Huot et al. 1999; Iwakura et al. 2002; Liang et al. 1998; Revesz et al. 2006; Tessier and Akiba 1999; Varin et al. 2006; Yu et al. 2002; Zaluska et al. 1999). Most past research studies of magnesium particles have been conducted based on powders processed by conventional ball milling due to their ability to change the microstructure of material. However,
the major disadvantages of mechanical ball milling are the excessive milling time required (30-60 hrs) (Doppiu et al. 2004; Huot et al. 1995; Tessier and Akiba 1999; Yu et al. 2002) and the formation of undesirable alloys. Varin et al. (2006) reported that after 20 hrs of milling, formation of Mg$_2$Ni alloy was observed, which results in a lowered hydrogen absorption capacity. In addition, it is challenging to control the shape and consistency of the product (Hong and Kim 2001; Hong et al. 2000; Yoshinaga et al. 1997). Therefore, a new milling system is desired which has significantly reduced operating time and is capable of reducing grain size without the formation of metal alloys.

Furthermore, a better understanding of the overall process of hydrogenation is needed to further develop the practicality of magnesium as a storage option. To explain the change of the rate limiting mechanisms in hydride formation, Jeon et al. (2007) experimentally demonstrated that formation of a MgH$_2$ layer starts from the outer layer of particle surface and grows into the bulk. Thus, in the beginning of the process, MgH$_2$ nucleation is the rate limiting mechanism; however, hydrogen diffusion through the impermeable hydride layer eventually becomes the rate-liming mechanism once the hydride layer reaches a critical thickness. The maximum penetration depth for nucleation limited condition for the tested sample was calculated to be 6 μm, i.e. if the layer is less than 6 μm, diffusion barrier is not longer a critical problem (Jeon et al. 2006). Since a short fueling time is critical to practical applications, it is advantageous to accomplish the majority of hydrogen uptake while it is in the most rapid nucleation-limited stage. In order to reduce the limiting effect of diffusion through the compact MgH$_2$ layer and thereby extend the nucleation-limited stage, particles with a high specific surface area and a narrow thickness are highly favored as they maximize surface reaction sites and minimize the
diffusion depth. Nano-sized Mg particles and thin Mg films have been used to minimize this problem; however, practical production costs of these materials may be a concern.

Additionally, the effect of geometry on the hydrogen absorption kinetics of magnesium particles has not yet been explored in depth. Development of new material production technologies that improve material utilization and increase production efficiency is very much sought after. Recently, a high speed orbiting ball media (HSOBM) processor was successfully introduced as a fast and efficient method to fabricate flake-shaped magnesium particles with a high specific surface area and a narrow thickness specifically for use as hydrogen storage materials (Theodore et al. 2006).

The objective of this chapter was to maximize the nucleation-limited regime, to improve material utilization and to enhance hydrogen uptake by changing either geometry or grain size of Mg. Spherical particles and flake particles were characterized to measure grain size and to evaluate its effect on hydrogenation. The HSOBM processor was also tested for its ability to coat the nano-catalyst on magnesium flakes in order to evaluate its potential for combined flake/coating processor. The coating efficiency of both the HSOBM processor and Theta Composer were assessed. Finally, the effects of geometry on hydrogen absorption kinetics were analyzed from hydrogenation data.

**Experimental Methodology**

**Fabrication of Magnesium Flake–Nano Nickel Composites**

Mg flakes were prepared using a HSOBM processor described in Chapter 4. The coating of nano Ni catalysts was carried out using either a HSOBM processor or a Theta Composer (Tokuju, Corp.) under an argon environment. In-depth details of the mechanistic aspects of the processes have been described elsewhere (Coowanitwong et al. 2003; Jeon et al. 2006; Theodore et al. 2006), and only a brief description is provided here.
The Theta Composer consists of an elliptic rotor encased in a vessel. The rotor operates at high revolution while the vessel counter-rotates at a lower speed. During rotation it applies strong compression and shear forces to the particles as they pass through the narrow gap between the rotor and vessel wall (Cooper et al. 2005; Coowanitwong et al. 2003; Jeon et al. 2006). The process also more evenly distributes the Ni nanoparticles onto the magnesium surface. The rotor and vessel are made of stainless steel in order to maintain an inert environment and prevent chemical reactions. The HSOBM processor uses ball media rolling on the walls inside a tube at high speed to create strong compression and shear forces, flattening particles as they pass between the rolling media and the vessel wall. In a likewise manor, the high speeds and large compression and shear forces are capable of breaking up nano-agglomerates and coating the nanoparticles on the Mg flake.

The basic procedure used in creating Mg-Ni flake composites is as follows: 25 mg magnesium (Fisher Scientific, 294 μm) and 6.0 mm balls (Chromium-Steel Cr-52100, Norstone Inc.) were introduced into the HSOBM tube in a glove box (oxygen level was lower than 0.5 ppm). The milling system was operated with an orbiting speed of 13,000 RPM, and with 2-min milling time. After each milling process, 3 wt. % of the nano Ni (primary particle size: 72 ± 30 nm, surface area: 6 m²/g, bulk density: 0.66 g/cm³, Argonide) was added to the Mg flakes. Then, the mixture was coated for 2 minutes with ball speeds of 13,000 RPM in the HSOBM (2.0 mm ball sizes) or for 90 minutes with the Theta Composer running at 4600 × 70 rpm.

The surface area analysis was performed on a Quanta Chrome NOVA 1200 Gas Sorption Analyzer using N₂ adsorption isotherm with a multi-point Brunauer-Emmett-Teller (BET) method. Scanning Electron Microscopy (SEM, JEOL JSM 6335F) coupled with Energy Dispersive Spectroscopy (EDS) was used for comparing surface morphologies on the
magnesium powders before and after the milling process and dispersion of nanocatalysts on the surface of Mg flake. To determine the thickness of the flake particles, they were suspended and solidified in an epoxy resin. The dried epoxy was then sliced transversally to obtain cross sectional slices of flakes suspended in the epoxy and subsequently examined under an optical microscope (Olympus BX-60). The formation of MgH$_2$ in the Mg–Ni flakes composites, the orientation of crystal structure and the grain refinements and lattice strains of flakes were determined by X-ray diffraction (Phillips XRD APD 3720) with a 2$\theta$ range of 20-70° with three seconds of count time per step.

**Hydrogen Absorption/Desorption Characterization**

Hydrogen absorption experiments were carried out in a hydrogenation system. The hydrogenation system is shown in Figure 5-1. 0.905 g of the Mg–Ni flake composite was introduced into the hydrogenation chamber while in a glove box. The chamber was flushed three times with argon to minimize possible contamination. In vacuum, the hydrogenation chamber was heated to the target temperature (483 K). Pure grade hydrogen (4.8) was then instantly introduced into the hydrogenation chamber at 1 MPa and hydrogen pressure was maintained constant in the chamber. The temperature of the chamber was monitored by a thermocouple (Fisher Scientific model 15-078-39, type K) and the hydrogen pressure in the reservoir was monitored using an electronic pressure transmitter (Omega, PX880).

After the hydrogenation process, the Mg-Ni flake composites were analyzed by a Thermo Gravimetric Analyzer (TGA 2050, TA Instruments) to determine the amount of hydrogen adsorbed in the Mg–Ni flake composites. The PV/RT value was utilized to aggregate pressure and temperature effects simultaneously and used to compare experimental data to theoretical prediction. The PV/RT data, calculated from the measured pressure loss, were accurate to within 1.5 % of the experimental data from TGA (Jeon et al. 2006), and were used in this study.
Although there are many parameters that affect hydrogen absorption/desorption rate, two of the more important parameters, namely change in particle geometry and Ni loading, were evaluated and other conditions were kept constant in this study. The experimental conditions are listed in Table 5-1.

Results and Discussion

Determination of Minimum Ni Loading

Prior to experimentation, the minimum nano Ni loading for spherical and flake-shaped particles was theoretically investigated. A minimum nano Ni wt. % is defined as the Ni wt. % required to form monolayer coverage on the surface of Mg powder. For spherical/flakes particles, the minimum Ni loading can be expressed by Equation 5-1 and Equation 5-2 respectively:

\[
X_{\text{sph}} = \frac{1}{\frac{1}{\pi} \left( \frac{d_m}{d_n} \right) \left( \frac{\rho_m}{\rho_n} \right) + 1}
\] (5-1)

\[
X_{\text{fla}} = \frac{1}{\frac{3}{\pi} \left( \frac{d_m h}{d_n (d_m + 2h)} \right) \left( \frac{\rho_m}{\rho_n} \right) + 1}
\] (5-2)

The definition of each parameter is listed in the Nomenclature section.

The average thickness and radius of flakes, measured to be 11.73 μm and 442 μm respectively under optical microscopy (Olympus BX-60) (Theodore et al. 2006), were used in this calculation. For 70 nm Ni, \( X_{\text{fla}} \) was founded to be 3.14 wt. % for flakes while \( X_{\text{sph}} \) was calculated to be 2.1 wt. % for the 44 μm Mg. Thus, Nickel loading in excess of 3 wt. % was not considered. Furthermore, loss in hydrogen capacity resulting from a heavier weight could render
the materials less desired for onboard storage (Chalk and Miller 2006; DOE 2007; Zaluska et al. 1999).

**Characterization of Mg Flakes (SEM/BET/XRD)**

Geometric examination of the magnesium powders before and after the HSOBM process was conducted using SEM. By comparing the images of pure 294 μm Mg and Mg flakes in Figure 5-2 (a) and (b), it was observed that after milling with HSOBM, Mg showed observable physical changes (i.e. evidence of cracking or formation of surface roughness) and reduction of thickness. Specific surface area of the powders before and after processing in the HSOBM was also measured using BET; however, the surface area was of too low magnitude (< 0.5 m²/g) to have reliable results.

The XRD spectra of the structural evolution of pure Mg are shown in Figure 5-3 (b) and (c). After 2 min milling with HSOBM, the 1st highest peak (36.6°) for pure Mg was significantly reduced in intensity. On the other hand, the intensity of the 2nd highest peak for pure Mg reached a significant peak after 2 min milling using the HSOBM processor. It was noted that the orientation of crystal structure of Mg, shown in Figure 5-3, was changed from 36.6° (orientation: 101) to 34.5° (orientation: 200). This could be due to plastic deformation resulting from shear/compression forces experienced by Mg during the HSOBM milling process (Callister 1997; Theodore et al. 2006) which would result in a change in the orientation of crystal structure. The change in turn caused grain refinement of Mg flakes and change of lattice strains. The grain refinements and lattice strains of Mg flakes for 34.5° (orientation: 200) peaks were also determined by single line profile analysis (Skoog et al. 1998) in addition to XRD. It was observed that the average gain size of flakes (316.3 nm with 0.26 % lattice strain) with two minutes of processing time was smaller than those of 294 μm Mg powder (423.4 nm with 0.19 %
lattice strains). The average grain size of 44 μm Mg powder is 132.3 nm with 0.16 % lattice strain.

The crystalline phase of Mg and Ni was preserved during processing and coating by HSOBM and Theta Composer, and no XRD peaks of Mg₉Ni₅ alloy were observed, as shown in Figures 3 (a), (d), and (e). After hydrogenation, the formation of MgH₂ was observed in samples 1, 4, and 5. In short, the HSOBM processor is able to fabricate smaller grain size with higher lattice strains with a short processing time.

Effect of Grain Size on the Hydrogen Absorption Kinetics without Nano Catalyst

Several studies (Dornheim et al. 2007; Dornheim et al. 2006; Huhn et al. 2005; Zaluska et al. 2001) have reported that the reduction of grain size increases the number of paths for hydrogen diffusion as well as nucleation sites for reaction, which altogether enhances hydrogen absorption kinetics. Past studies have shown that particles with nano-sized grains, which have been mechanically milled for long periods (greater than 300 hours), have appreciable hydrogen absorption without the need for catalysts while also reacting at relatively low temperatures (Dornheim et al. 2007; Huhn et al. 2005). To investigate the effects of average grain size of Mg powder before and after milling on hydrogen absorption capacity, 294 μm spherical Mg powders were milled for 2 minutes to form 442 μm flakes (with 11.7 μm thickness). Hydrogenation tests were performed for these samples that had no Ni catalyst coating. Figure 5-4 shows the effects of grain size on the hydrogen absorption capacity. Although the thin flake-shaped particle had smaller grain size, as shown, there was no evidence of hydrogen absorption in either of the pure Mg samples. Therefore, it can be inferred that in the absence of Ni catalysts the reduction of grain size produced by the HSOBM processor has negligible effect on hydrogen absorption capacity. This confirms the precedence of the Ni catalyst for feasible hydrogen absorption on Mg particles. It also shows a deviation from previous studies which indicated that powders with
reduced grain sizes hydrogenated without the aid of nano catalysts (Dornheim et al. 2007; Huhn et al. 2005). The most likely reason for this deviation is that the flake samples did not have a sufficiently small grain size (100 nm) because of the short milling time which was constrained by the mechanical endurance limitations of the device.

**Analysis of Coating Methods and Change of Thickness**

The effective dispersion of catalysts and geometry change were also investigated with two dry coating methods (HSOBM and Theta composer). Figure 5-5 shows a homogeneous distribution of nano Ni on the Mg powder/flake surface under SEM-EDS. The dispersion of nano Ni was further assessed quantitatively using Spot Advanced (Diagnostic Instrument, INC) image capture software (Coowanitwong et al. 2003; Oh et al. 2001; Theodore et al. 2006). Thirty equally divided areas were randomly selected from the EDS images of Ni on the Mg substrate. The number of individual Ni clusters was determined in each area and statistical analyses were performed. It is observed from Figure 5-6 that 2 min coating with HSOBM yielded Ni clusters that were larger in size but fewer in number with a lower mean and standard deviation (23.7 and 5.59, respectively) as compared to that of Theta Composer with 90 min coating time (50.76 and 8.76, respectively). Figure 5-6 also shows that 44 µm Mg coated with Theta Composer yielded Ni clusters with a similar mean and standard deviation (55.4 and 8.10, respectively) as compared to Mg flakes with Theta composer (50.76 and 8.76, respectively). This comparative analysis confirmed that Ni nanoparticle dispersion was more effective with Theta composer. This is mostly a result of the short operating time of the HSOBM device as well as its high coating speeds which have been known to subdue coating efficiency due to a nano-lubrication effect (Bowden and Tabor 1986; Hsu 2004).

Thickness change was measured after Theta Composer and HSOBM coating under optical microscope (Olympus BX-60). The average thickness of flakes (sample 3 and sample 4)
was 11.73 μm and 11.76 μm, respectively, after coating with HSOBM. After Theta Composer coating the average thickness of flakes (sample 5) increased from 11.73 μm to 16.87 μm.

**Effect of Dispersion of Nano Catalysts on Hydrogen Absorption Kinetics**

Figure 5-7(a) plots the hydrogen absorption data for samples 1, 4 and 5, as a function of time. It can be seen that the least effective material was sample 4, which was a flake particle using the HSOBM coating method. Its poor performance is most likely due to insufficient catalytic enhancement and is supported by the lower coating quality reported in section 3.4. Samples 1 and 5 were coated using the more efficient Theta Composer and showed significant hydrogen absorption capacities of 4.19 wt. % and 4.62 wt. % respectively, after 300 minutes. The hydrogen absorption capacities for samples 1, 4 and 5 were also confirmed using TGA analysis and can be seen in Figure 5-7(b). This analysis supports the trend that hydrogen absorption capacity is largely dependant on an effective Ni catalyst coating. In order to appreciate the effect of surface area for each sample’s results, the specific surface area of each sample was estimated assuming spherical particles or smooth flakes of uniform thickness and diameter. The results gave that samples 4 and 5 shared relatively close specific surface areas to sample 1, with ratios of 1.31:1 and 0.931:1. It can therefore be reasonably inferred that difference in surface area had negligible impact on the observed trends.

**Effect of Geometric Change on Hydrogen Absorption Kinetics**

To closely observe the effect of coating efficiency and particle geometry on kinetics, a hydrogen absorption rate vs. metal hydride volume fraction plot is rendered in Figure 5-8. The initial observations support earlier conclusions that sample 5 shows the highest initial absorption rate followed by sample 1, and the lowest absorption rate by sample 4. When α is approximately 0.28, the rate of absorption for well coated flakes was approximately four times that of poorly
coated flakes. Coating efficiency can therefore be seen to drastically affect the kinetics when comparing flakes-shaped particles.

The effect of particle geometry on kinetics can also be observed between samples of spherical and flake particles which were both effectively coated with Ni catalyst. Compared to sample 1 of spherical particles, sample 5 clearly shows a shift towards higher reaction rates and capacities. This shift of the sample regression lines towards higher hydrogen absorption can be understood as an increase in the critical hydrogenation capacity ($\Psi$). $\Psi$ is defined as the point at which the hydrogen absorption kinetics switch from the nucleation-limited to diffusion-limited regime and is estimated by the intersection of the tangential lines coming from the beginning and ends of the sample regression lines. In fact, the change in geometry from the spherical to the flake-shaped particle extends the nucleation-limited period, which is more favorable since its kinetics is faster than that of the diffusion-limited regime. This ultimately leads to a higher absorption capacity in a given period of time for flake-shaped particles, as observed in Figure 5-7. This same analysis also supports the poor results of sample 4, as its regression line is shifted towards lower hydrogen absorption area in Figure 5-8. This is known already to be a result of poor coating efficiency, which is evident when compared with sample 5 of the same geometry.

The observed effects of particle geometry on hydrogen absorption can be reasonably understood based on a simple macroscopic comparison of hydrogen diffusion under rectangular (flake particles) vs. radial (spherical particles) coordinates. For rectangular coordinate systems, as hydrogen diffuses into the Mg flake, the flux area remains relatively constant with respect to the hydrogen penetration depth. However, for spherical particles understood through a radial coordinate system, as the hydrogenation layer thickens, the available flux area reduces with decreasing radius. This results in a diffusional term which reduces as a function of time and
subsequently brings upon a diffusion-limited case earlier than in the rectangular coordinate system.

Previous research has emphasized that the grain size of the particle is also an important factor in hydrogenation (Dornheim et al. 2007; Dornheim et al. 2006; Zaluska et al. 2001). For sample 1, the grain size was significantly smaller than that of the flakes in sample 5, implying that the hydrogen absorption capacity and rate of the spherical 44 μm particles should be much better than that of the flakes. Since this was not the result in this study, it is therefore inferred that the effect of geometry on hydrogen capacity and absorption rate is dominant over the effect of grain size. Ultimately, these results show that the flake particle which had nearly equal coating efficiency and specific surface area as that of the spherical 44 μm sample exhibited improved absorption kinetics and capacities over spherical particles.

**Summary**

This study aimed at improving hydrogen storage density characteristics of magnesium so as to enhance hydrogen uptake kinetics and storage efficiency by utilizing thin Mg flakes with large diameters coated with nano-Ni catalysts. XRD analyses of the product processed by the HSOBM process showed a change in the orientation of crystal structure of Mg and a reduction in grain size; however, this change was not large enough to hydrogenate pure Mg flakes. The individual crystalline phase of Mg and Ni was preserved and no XRD peaks of Mg₆Ni₇ alloy were observed after processing with the HSOBM processor or when coating with Theta composer. Comparisons between samples of flakes without Ni coating, and with coating by the HSOBM processor and Theta Composer confirmed the need of well dispersed nanocatalysts particle for practical hydrogenation systems.

Hydrogenation absorption trends showed that flakes had longer nucleation-limited periods than spherical particles, which lead to higher initial absorption rates and higher final
absorption capacities. Geometry was identified to be a critical factor affecting hydrogen absorption capacity and kinetics, and was dominant over the effects of grain boundary.

**Nomenclature**

- $d_m$: Diameter of Mg [m]
- $d_n$: Diameter of Ni [m]
- $h$: Initial thickness of Mg flakes [m]
- $X_{sp}$: Minimum wt. % of catalyst for spherical particle [wt. %]
- $X_{fla}$: Minimum wt. % of catalyst for flake particle [wt. %]

**Greeks**

- $\alpha$: Metal hydride volume fraction [-]
- $\rho_m$: Molar density of Mg particle [mole/m$^3$]
- $\rho_n$: Molar density of Ni particle [mole/m$^3$]
- $\Psi$: Critical hydrogenation capacity [-]
<table>
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<tr>
<th>Sample</th>
<th>Particle size and shape</th>
<th>Ni (wt.%)</th>
<th>Milling time (min)</th>
<th>Coating time (min)</th>
<th>Predicted (wt. %)</th>
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<td>294 ±155 µm Mg sphere</td>
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</tr>
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<td>0</td>
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<tr>
<td>4</td>
<td>438 ±328 µm Mg flakes</td>
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<td>2*</td>
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<td>3</td>
<td>2</td>
<td>90**</td>
<td>4.62</td>
<td>4.57</td>
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* coating method: HSOBM
** coating method: Theta Composer
Figure 5-1. Schematic diagram of hydrogenation system
Figure 5-2. Surface morphology change: (a) sample 2 (pure 294 µm Mg, 180x); (b) sample 3 (Mg flakes, 180x); (c) sample 5 after Theta Composer (294 µm Mg - Ni composites, 2000x); (d) sample 4 (Mg flake-Ni composites, 2000x)
Figure 5-3. Comparison of XRD patterns: (a) sample 4 after hydrogenation; (b) sample 2 before HSOBM processing; (c) sample 3 after 2min HSOBM processing; (d) sample 1 after hydrogenation; (e) sample 5 after hydrogenation
Figure 5-4. Effect of morphological change on the hydrogen adsorption kinetics (w/o catalysts, experiment)
Figure 5-5. Distribution of Ni nano particles on Mg (a) SEM image (sample 1); (b) Ni mapping (sample 1); (c) SEM image (sample 4); (d) Ni mapping (sample 4); (e) SEM image (sample 5); (f) Ni mapping (sample 5)
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CHAPTER 6
CONCLUSIONS AND RECOMMENDATIONS

Over the past decade, the increasing demands for clean energy to reduce global warming and to secure the future’s needs amidst the tremendous increase in energy consumption have led researchers to call for the development of new alternative energy sources. This study was carried out to investigate Mg-nano Ni composites as an alternative for solid hydrogen storage with high volumetric/gravimetric capacity. The kinetics and capacity of magnesium hydride formation on Mg-nano Ni composites synthesized by the Theta Composer as well as a high speed orbiting ball media (HSOBM) processor were characterized and evaluated for three key parameters for its practical application: dispersion of nano catalysts over Mg powder surface, the change of rate limiting mechanism, and the change of geometric shape of Mg powder.

First, the formation of magnesium hydride on Mg-Ni composites synthesized by Theta Composer was investigated. It was observed that there was a change in the rate limiting mechanism of hydrogenation from chemical absorption on the surface of the Mg particle to diffusion through the hydride layer into the Mg particle core. A longer coating time in Theta Composer improved the hydrogen storage capacity and absorption/desorption rates for composites with the same Ni loading wt % due to the improved distribution of Ni nanocatalysts. However, after the rate limiting mechanism changed from chemical absorption to H₂ diffusion, Ni wt % loading had negligible impact on the H₂ absorption rate and capacity. Regarding how hydride was formed, the SEM/TEM characterization verified that magnesium hydride layer formed from the surface rather than from random nucleation and growth in Mg. This observation provides an insight into the partitioning of the rate limiting mechanism between interfacial growth and diffusion, and it forms the basis for the analytical model.
The newly developed analytical model considered multiple mechanisms and a variable hydrogen concentration. The agreement between modeled and experimentally measured data was excellent, and the model was successfully demonstrated to be able to evaluate the change of rate-limiting mechanisms of Mg-Ni composites with regards to hydrogen absorption rate and capacity.

To improve hydrogen storage density characteristics and to enhance hydrogen uptake kinetics and storage efficiency, thin Mg flakes with large diameters coated with nano-Ni catalysts were proposed. The Mg flakes were fabricated by a high speed orbiting ball media (HSOBM) processor and were effectively coated with Ni nanocatalyst using the Theta Composer. Comparisons between samples of flakes without and with Ni coating by the HSOBM processor and Theta Composer confirmed the need of well dispersed nanocatalyst particles. Hydrogen absorption trends showed that flakes had longer interfacial growth-limited periods than spherical particles with similar specific surface area. The difference led to higher initial absorption rates and larger final absorption capacities. Geometry was identified to be a critical factor affecting hydrogen absorption capacity and kinetics, and was dominant over the effects of grain boundary.

Based on the knowledge learned and the experiences gained in this research, recommendations are made to help further advance the application of Mg-nano Ni composite.

1. A higher heating rate is beneficial to a substantial improvement in hydrogen absorption rate and storage capacity. The effect of higher heating rate on hydrogen absorption requires further investigation. A thermally insulating chamber and an automatic temperature control system can be used to improve uniformity of temperature profile as well as the stability of heating rate in the chamber.

2. The analytical model developed in this study accurately described hydrogen absorption capacity and kinetics, as it accounts for the effects of important mechanisms: interfacial growth of metal hydride and diffusion of hydrogen. To further expand the applicability of the
model, the effects of heating rate and geometric change of Mg powder on the hydrogen absorption should be included.

3. Due to the mechanical endurance limitations of the current HSOBM system, investigation of the effects of milling time couldn’t be extended to more than 2 minutes. A new system that can overcome the existing barrier needs to be developed. The application of the HSOBM processor can then be further explored for thinner (< 10 µm) Mg flakes or other materials.

4. Further studies to understand the formation of magnesium hydride layer on Mg-Ni composites fabricated by the HSOBM processor will embellish these results.

5. The microstructure of magnesium hydride on Mg-Ni composites fabricated by the HSOBM processor and Theta Composer should be further studied using electron microscopy and X ray diffraction. This kind of study will allow us to better understand the structural evolution that occurs during absorption and desorption. Such information will help us better understand the phase transformations and eventually propose further enhanced designs of hydrogen storage materials.
APPENDIX
EFFECTS OF PRIMARY PARTICLE SIZE AND INITIAL GEOMETRIC STANDARD DEVIATION ON BROWNIAN COAGULATION OF FRACTAL NANOAGGLOMERATES IN THE FREE MOLECULAR REGIME

Introduction

Coagulation is one common process encountered in the commercial production of specialty materials, such as catalysts, medicine, cosmetics, food, plastic, as well as energetic and other advanced materials (Friedlander and Pui 2004; Pratsinis 1998; Stark and Pratsinis 2002; Yang and Biswas 1997). By nature, particles made by high temperature gas-to-particle conversion followed by coagulation are agglomerates composed of nanoparticle chains (Pratsinis 1998; Schmidt-Ott 1988). Applications of tailored nanoparticles are mushrooming and there have been many studies in recent years to understand the synthesis process and to control the properties.

Experiments have been attempted to study the characteristic behavior of Brownian coagulation processes with agglomerates. For example, Matsoukas and Friedlander (1991) reported that the coagulation rate of metal oxide particles produced by flame synthesis increased with decreasing mass fractal dimension and primary particle size. It should be noted here that the primary particle size of commercially available TiO$_2$ agglomerates in diffusion and premixed flame reactors varies from a few nm to 20 nm (Degussa AG, TI 1234; Pratsinis 1998). Akhtar et al. (1991) showed that nonspherical titania agglomerates grew much faster than spherical particles and they approached an asymptotic mass fractal dimension during high-temperature oxidation. Monte-Carlo simulations have also been widely used to explain the morphological evolution of agglomerates undergoing various processes – such as diffusion (Oh et al. 2002), sintering and coagulation (Akhtar et al. 1994). Mountain et al. (1986) introduced a stochastic simulation algorithm. The trajectory of a primary particle was tracked by solving the Langevin equation coupled with a periodic boundary condition to calculate how deterministic and
stochastic forces act on a particle in motion. Meakin et al. (1986) proposed a computational algorithm to simulate the agglomeration process. According to the proposed mechanism, morphology of agglomerates can be classified into two types: diffusion-limited and reaction-limited (Schaefer 1988).

Aerosol dynamics models have also been developed to identify the effects of morphological structure on the behavior of these agglomerates. There are several types of aerosol models available to describe aerosol dynamic processes based upon their mathematical description of size distribution function, such as moment (Frenklach and Harris 1987; Lee and Chen 1984; Whitby 1979) and sectional models (Gelbard and Seinfeld 1980; Landgrebe and Pratsinis 1990). Wu and Friedlander (1993) simulated the evolution of agglomerates starting with individual spherical particles assuming a power law distribution and examined the effects of fractal dimension and primary particle size. Vemury et al. (1994) proposed self-preserving time-lag as a useful tool to express the time it takes to reach the asymptotic size distribution. Two correlation equations were developed for the self-preserving time-lag in the free molecular and continuum regimes as a function of initial geometric standard deviation. The calculations were implemented using a discrete-sectional model. In the follow-on study (Vemury and Pratsinis 1995), mass fractal dimension was incorporated into the model to examine its impact.

Lee et al. (1990) derived the first analytical solution to track the size distribution evolution of a lognormally distributed spherical aerosol undergoing Brownian coagulation in the free molecular regime. Park and Lee (2002) recently expanded the analytical solution to include fractal agglomerates, which focused on the change of self-preserving time-lag as a function of mass fractal dimension. The sectional model (Landgrebe and Pratsinis 1990) and analytical solution (Park and Lee 2002) were compared for the predicted shape of the asymptotic
agglomerate size distribution. Numerically predicted asymptotic values by the sectional method for $D_f$ of 3.0, 2.5, and 2.0 were 1.462, 1.519, and 1.610, respectively, while the analytical solutions obtained by Park and Lee’s study (2002) were 1.355, 1.393, and 1.481, respectively. A caveat of both studies is that they did not evaluate the effect of primary particle size. The size of primary particles has been identified as an important variable from previous experimental studies described in the preceding text. Further affirmation of the importance of primary particle size was provided by Ulrich and Subramanian (1977) who described the behavior and physical properties of agglomerates generated from high-temperature gas phase process. They reported that the properties were highly dependent on the number and size of primary particles and the agglomerate size.

As pointed out in these prior studies, the time to reach asymptotic distribution is of great interest to nanoparticle synthesis. The objective of this study, therefore, was to develop a formula for self-preserving time-lag that incorporates all important parameters of nanoagglomerates, including primary particle size, geometric standard deviation and fractal dimension. This study focused on the influence of primary particle diameter, which was pointed out to affect coagulation rate although the effects have not been investigated by previous aerosol dynamic models. The study further examined the influence of the other two parameters on the effect of primary particle size.

**Model Development**

To describe the particle size distribution undergoing Brownian coagulation, an integro-differential equation (Friedlander 2000) was used, which can be expressed as

$$\frac{\partial n(v_j, t)}{\partial t} = \frac{1}{2} \int_0^{v_j} \beta(v_i, v_j - v_i) \times n(v_j, t) \times n(v_i - v_j, t) dv_i - n(v_j, t) \int_0^\infty \beta(v_i, v_j) \times n(v_i, t) dv_i \quad (1)$$
where \( n(v_j, t) \) is the particle size distribution function at time \( t \) and \( \beta(v_i, v_j) \) is the collision kernel for two particles having \( v_i \) and \( v_j \) volume, respectively. The collision kernel in the free molecular regime is

\[
\beta(v_i, v_j) = \pi \left( d_{ai} + d_{aj} \right)^2 \left( \frac{k_b T}{2 \pi \rho} \right)^{1/2} \left( \frac{1}{v_i} + \frac{1}{v_j} \right)^{1/2}
\]

where \( \pi (d_{ai} + d_{aj})^2 \) is the collision cross section for agglomerates and \( (k_b T/2 \pi \rho)^{1/2}[1/v_i + 1/v_j]^{1/2} \) is the average relative velocity between colliding agglomerates.

For fractal aggregates with a fractal dimension \( (D_f) \), the relationship between the primary particle diameter \( (d_p) \) and the radius of gyration of the agglomerate \( (R_g) \) is related to the number of primary particles in the agglomerate \( N_{pp} \) as (Wu and Friedlander 1993)

\[
N_{pp} = \frac{v}{v_0} = k \left( \frac{2 R_g}{d_p} \right)^{D_f}
\]

where \( v_0 \) is the volume of the primary particle and the prefactor \( k \) is called the structure factor (Mandelbrot 1982).

If the fractal dimension of agglomerates is between 2 and 3, the planar projections of the agglomerate cross sections are given by

\[
cross \ section \ \propto (R_{gi} + R_{gw})^2
\]

Without a limit for \( D_f \), there would arise the anomaly wherein the cross-section of the new agglomerate would be larger than the sum of the cross-sections of the individual agglomerates. Therefore, a limit of \( D_f \geq 2 \) has been suggested. Moreover, it is assumed that \( D_f \) is a constant, said assumption being supported by computer simulations (Friedlander 2000). Incorporating Equations 2 and 3 with \( k \) set to 1, the collision kernel for agglomerates can be expressed by the
gas kinetic theory for rigid spherical particles for $D_f > 2$ in the free molecular regime (Matsoukas and Friedlander 1991) as

$$\beta(v_i, v_j) = K \left( \frac{1}{v_i} + \frac{1}{v_j} \right)^{\frac{1}{2}} v_i^{1/D_f} + v_j^{1/D_f}$$

(5)

where $K = \left( \frac{6k_b T}{\rho} \right)^{\frac{1}{2}} \left( \frac{3}{4\pi} \right)^{2/D_f - 1/2} \left( \frac{d_p}{2} \right)^{2-6/D_f}$, $k_b$ is the Boltzmann constant, $T$ is the absolute temperature, and $\rho$ is the particle density.

Due to the efficient structure and low computational demand, the moment method has been widely used to explain the coagulation phenomena (Whitby and Atmospheric Research and Exposure Assessment Laboratory (U.S.) 1991; Williams and Loyalka 1991). The $k_{th}$ moment of the particle size distribution is written as

$$M_k = \int_0^\infty v^k \cdot n(v, t) dv$$

(6)

The moment model assuming a lognormal size distribution was used in this study where the distribution function is written as

$$n(v, t) = \frac{1}{3v} \frac{N(t)}{\sqrt{2\pi} \ln \sigma_g(t)} \exp \left[ -\ln^2 \left( \frac{v}{v_g(t)} \right) \right]$$

(7)

where $N(t)$ is the total number concentration of particles, $\sigma_g(t)$ is the geometric standard deviation and $v_g(t)$ is the geometric number mean particle volume. By incorporating Equation (1) with Equations (6) and (7), the various moment equations can then be derived. The development of the moment method was provided in detail in Park and Lee (2001) for the derivation of the analytical solution, and thus is not repeated here. The three differential equations for the moments used in this work, solved numerically using a Runge-Kutta 4th order method, are
summarized in Table 1 and they are for comparison purposes only. Once the moments are determined for each time step, the key size distribution parameters (i.e., geometric standard deviation and geometric mean diameter) can be then determined. In deriving the analytical solution, Park and Lee (2002) made several assumptions. These assumptions are no longer needed when solving these equations numerically.

**Simulation Conditions**

Primary particle size, mass fractal dimension and initial geometric standard deviation were varied to evaluate the effects of agglomerate size distribution on coagulation rate. The conditions are summarized in Table 2. The evolution of $\sigma_g$ was tracked to determine the time to reach the asymptotic state, i.e., self-preserving time-lag for fractal nanoagglomerates, $\tau_f$. Following the convention of prior studies, $\tau_f$ is defined as the time it takes for $\sigma_g$ to approach within 1 % of the asymptotic value (Landgrebe and Pratsinis 1990; Vemury et al. 1994; Vemury and Pratsinis 1995). The simulation conditions of Set 1 were the same as in Vemury and Pratsinis (1994) and Park and Lee (2002), so that the results could be compared with those of previous studies. In Sets 2 and 3, $d_p$ and $\sigma_{g0}$ were varied to investigate the dependence of $\tau_f$ on these parameters.

**Results and Discussion**

**Effects of $D_f$ and $d_p$ on coagulation rate**

Before the simulation was carried out, the impact of $D_f$ and $d_p$ on the dynamics of agglomerate growth was investigated. This was done by examining the relationship between the collision kernels of agglomerates ($\beta_a$) and spherical particles ($\beta_s$) of the same particle volume. For nonspherical particles, $\beta_a$ is expressed by Equation (5). For spherical particles, by setting $D_f = 3$,
\[
\beta_s = \left( \frac{6k_b T}{\rho} \right)^{1/2} \left( \frac{3}{4\pi} \right)^{1/6} \left( \frac{1}{u} + \frac{1}{v} \right)^{1/2} \left( u^{1/3} + v^{1/3} \right)^2
\]  
(8)

Dividing Equation (5) by Equation (8), the ratio can be derived as

\[
\frac{\beta_a}{\beta_s} = \left( \frac{3}{4\pi} \right)^{1/2} \left( \frac{d_p}{2} \right)^{2-6/D_f} \left( \frac{v^{1/D_f} + u^{1/D_f}}{v^{1/3} + u^{1/3}} \right)^2
\]  
(9)

Under either a monodisperse assumption \((u = v)\), or an extreme size ratio \((v \gg u)\), the ratio of the collision kernels can be expressed as:

\[
\frac{\beta_a}{\beta_s} = \left( \frac{3}{4\pi} \right)^{1/2} \left( \frac{d_p}{2} \right)^{2-6/D_f} \left( \frac{2R_g}{d_p} \right)^{(2-2/D_f)}
\]  
(10)

where \(v = \left( \frac{2R_g}{d_p} \right)^{D_f} \left( \frac{\pi}{6} d_p^3 \right)\) following Equation (3) where \(k\) is set to 1. As shown in Equation (10), agglomerates with a smaller primary particle size and a smaller mass fractal dimension are expected to have a higher collision rate.

**Effect of \(D_f\) on the asymptotic \(\sigma_g\)**

Prior studies (Park and Lee 2002; Vemury and Pratsinis 1995; Wu and Friedlander 1993) have reported that \(\sigma_g\) approaches an asymptotic value when coagulation is the dominant mechanism. Figure 1 shows the asymptotic \(\sigma_g\) determined in this work as well as the analytical solution reported by Park and Lee (2002). The results obtained by this study for fractal agglomerates, as shown, are almost identical to the analytical results (symbols overlapped in the figure) provided by Park and Lee (2002). The self-preserved geometric standard deviations for \(D_f = 3.0, 2.5\) and \(2.0\) were \(1.355, 1.393\) and \(1.481\) respectively. The similarity verifies that the effects of assumptions used in Park and Lee (2002) are negligible. The results by the discrete-sectional methods (Vemury and Pratsinis 1995; Wu and Friedlander 1993) are also presented.
Differences between the moment and the sectional models are due to the presumed size distribution. Therefore their asymptotic values, by nature, are different. Differences between the volume-based and number-based model results are due to the finite sectional spacing that yields numerical diffusion (Landgrebe and Pratsinis 1990; Wu and Biswas 1998).

**Effect of $d_p$ on $\tau_f$ and $\sigma_g$ as a function of $D_f$**

To investigate the effect of $d_p$ on $\tau_f$ and $\sigma_g$, simulation runs were performed for $d_p$ from 1 nm to 20 nm with all the other parameters kept constant. Figure 2a shows the results of asymptotic $\sigma_g$ as a function of $D_f$ for 3 primary particle sizes. As shown, the influence of $d_p$ is negligible (symbols overlapped) and all the asymptotic values are dependent on $D_f$ only. Different results are observed, however, for the effect on $\tau_f$, as shown in Figure 2b. The results are plotted in dimensionless time, $\tau_f$ following the definition by Vemury and Pratsinis (1995) as

$$\tau_f = \left( \frac{3k_b T d_p}{\rho_p} \right)^{\frac{1}{2}} \left( \frac{3}{4\pi} \right)^{\frac{1}{2}} N_0 t$$

(11)

where $t$ was obtained from the simulation runs.

As shown, when $d_p = 2$ nm, $\tau_f$ does not change much as $D_f$ varies. Besides, they agree well with those of the sectional method (Vemury and Pratsinis 1995) even though their asymptotic values ($\sigma_g$) are different. As $d_p$ and $D_f$ increase, however, the effect on $\tau_f$ becomes more prominent. At $D_f = 3$, $\tau_{20nm}$ is approximately 15 times larger than $\tau_{2nm}$, even though the asymptotic $\sigma_g$ value is the same for both (Figure 2a). Agglomerates composed of smaller primary particles tend to have greater drag forces and coagulate faster than their larger counterparts. Hence, they can reach the asymptotic value faster.
A statistical formula was then developed for $\tau_f$ as a function of $D_f$ for 2 nm primary particles. The formula was developed using one-way non-linear regression of an exponential relationship, which has the form as follows

$$\tau_{2nm} = \frac{1}{0.2734 + \exp\left(\frac{42.1}{D_f^2} - 11.8\right)} \quad (D_f \geq 2.0) \quad (12)$$

The choice of the exponent follows that implicated by Park et al. (2000). A good correlation was obtained with an $R^2$ of 0.9963. The formula was then compared with the time lag reported by Vemury and Pratsinis (1995). As shown in Figure 2b, the results between the discrete-sectional methods (Vemury and Pratsinis 1995) and moment method for 2 nm closely agreed.

**Combined effect of $d_p$ and $D_f$ on $\tau_f$**

The dependence of $\tau_f$ on both $d_p$ and $D_f$ was further evaluated statistically using two-way ANOVA and least square non-linear regression of an exponential relationship with a 95% confidence interval. To facilitate the analysis, normalized self-preserving time lag ($\tau_n$) was used in this study, which is defined in Equation (13) as the ratio of self-preserving time lag of agglomerates composed of any primary particle size ($> 2$ nm) to that for 2 nm primary particle with the same $D_f$:

$$\tau_n = \frac{\tau_f}{\tau_{2nm}} \quad (13)$$

The dependence of $\tau_n$ on $d_p$ and $D_f$ can then be expressed as

$$\tau_n = 1.079394 + 1.04 \times 10^{-5} e^{(0.268549 d_p + 2.835173 D_f)} \quad (R^2 = 0.9938) \quad (14)$$
The actual time lag for agglomerates composed of a given $d_p$ and $D_f$ can be derived by combining Equations (13) and (14) as

$$\tau_f = \left[ 0.079394 + 1.04 \times 10^{-5} e^{(0.268549d_p + 2.835173D_f)} \right] \left[ 0.2734 + e^{\frac{42.1}{D_f^{11.8}}} \right]$$ \quad (15)

Figure 3 shows the self-preserving time lag for various $D_f$ as a function of $d_p$. As shown, with a smaller $D_f$ (e.g. 2), $d_p$ does not seem to impose any significant effect. Values of the self-preserving time lag do not change much for the entire range of primary particle size. The effect of $d_p$ on $\tau_n$, however, becomes more prominent as $D_f$ increases.

**Integrated effect of $d_p$, $D_f$, and $\sigma_{g0}$ on $\tau_f$**

Similar to the previous section, the dependence of $\tau_f$ as a function of $d_p$, $\sigma_{g0}$ and $D_f$ was considered in the sequential statistical evaluation using three-way ANOVA and least square non-linear regression of an exponential relationship with a 95 % confidence interval. Figure 4 shows $\tau_f$ as a function of $\sigma_{g0}$ for 2 nm agglomerates. Vemury et al. (1994) proposed two correlation equations to predict $\tau_f$, based upon $\sigma_{g0}$: for $\sigma_{g0}$ smaller than the asymptotic value,

$$\tau_f = A\sigma_{g0} - B(\sigma_{g0} - 1)^2 \exp\left[- C(\sigma_{g0} - 1)^3\right]$$ \quad (16)

and for $\sigma_{g0}$ greater than the asymptotic value,

$$\log_{10} \tau_f = D + E\sigma_{g0}$$ \quad (17)

It should be noted that these formulae were based on $d_p = 2$ nm and $D_f = 3$. Formulae for other $d_p$ and $D_f$ are of great importance as discussed earlier,

The dependence of the time lag on these parameters for the moment model can be statistically derived. For $\sigma_{g0}$ smaller than the asymptotic value, the format of Equation (16) was
adopted, although the parameters A-C are no longer constants. For $\sigma_0$ greater than the asymptotic value, a new format is chosen as shown in Equation (18).

$$\tau_f = \exp(D + E \cdot \sigma_0) + F \quad (R^2 = 0.992)$$  \hspace{1cm} (18)

With a 95% confidence interval, it was found that each of the five variables ($A, B, D, E$ and $F$) in Equations (16) and (18) shows significant dependence on primary particle size and mass fractal dimension. Meanwhile, variable $C$ is only a function of mass fractal dimension. The dependence of $\tau_f$ on all these parameters was then examined by a 3-way ANOVA test with a 95% confidence interval. The 3-way regression relationship associated with the curve fits by the $R^2$ values has the factors (A-F) as listed below,

\[
A = 3.043 + 1.2 \times 10^{-5} \exp(3.337 \cdot D_f + 0.251 \cdot d_p) \\
B = -32.132 - 1.8 \times 10^{-4} \exp(3.352 \cdot D_f + 0.238 \cdot d_p) \\
C = -6.083 - 2.378 \exp(10 \cdot D_f^{-1}) \\
D = -42.067 + 17.139 \exp(0.204 \cdot D_f) + 4.549 \cdot \exp(0.033 \cdot d_p) \\
E = -2.288 + 18.952 \exp(-0.604 \cdot D_f - 0.014 \cdot d_p) \\
F = -2.043 \cdot \exp(-5.41 \times 10^{-5} \cdot D_f + 3.424 \cdot d_p) + 0.207
\]

Figure 5 shows the effect of $D_f$ and $\sigma_{g0}$ on $\tau_f$. As shown, the closer $\sigma_{g0}$ is to the asymptotic value, the shorter the self preserving time lag. The dependence between $\sigma_{g0}$ and $\tau$ shows an exponential relationship. Furthermore, it takes longer to reach the asymptotic value as the agglomerates become more compact (larger $D_f$). When the initial aerosols are monodisperse ($\sigma_{g0} = 1$), $\tau_f$ becomes $A$, which is a function of $d_p$ and $D_f$. While the formulae developed by Vemury et al. (1994) are good for 2 nm primary particles, particles produced in many industrial applications may very likely be of other sizes. With these three important parameters integrated into one equation, the new formula can be used as a convenient tool to predict the time it takes to reach the asymptotic state.
Implication to nanoparticle synthesis

For many industrial applications, the primary particle size synthesized is usually much larger than 2 nm. For example, Degussa P25 titania is produced by flame synthesis and its primary particle is around 20 nm (Degussa, AG, TI 1234); anatase TiO$_2$ nanoparticles synthesized by chemical vapor deposition of organic vapor precursors are between 12 and 23 nm (Backman et al. 2004; Miquel et al. 1993). Prior models (Park and Lee 2002; Vemury et al. 1994) are based on a primary particle size of 2 nm. The effect of $d_p$ is negligible for a small $D_f$ (e.g. 2). On the other hand, for a larger $D_f$ (= 3), as shown in Figure 4, $\tau_f$ increases exponentially as $d_p$ increases. According to Equation (17), it takes 20 nm primary particles 7 times longer than 2 nm primary particles to reach a self preserving distribution. The new formula can provide a more accurate estimate as it accounts for the effects of all important parameters: primary particle size, initial geometric standard deviation and the fractal dimension of the agglomerates.

Conclusion

The effects of primary particle size and initial geometric standard deviation on the change in geometric standard deviation and self-preserving time-lag of fractal agglomerates in the free molecular regime were investigated. In evaluating the effects of initial geometric standard deviation, results of the moment method were very close to those of the analytical solution. Meanwhile, sectional methods were not in as close an agreement in the asymptotic values due to the assumptions of the size distribution shape used in these models.

The dependence between $\sigma_{g0}$ and $\tau_f$ showed an exponential relationship with primary particle size, initial geometric standard deviation, and mass fractal dimension. The asymptotic geometric standard deviation did not depend on the primary particle size. When the mass fractal dimension was small ($D_f = 2.0$), the effect of primary particle size on the self preserving time lag
was negligible. Self preserving time lag decreases as the initial geometric standard deviation gets closer to the asymptotic value. Statistical formula for the dependence of self preserving time lag on primary particle size, initial geometric standard deviation, and mass fractal dimension of agglomerates were developed with high $R^2$ values (> 0.99). These statistical formulae incorporating the three important parameters serve as a convenient tool to estimate the self preserving time lag of fractal agglomerates.

**Nomenclature**

$R_g$ \hspace{1cm} radius of gyration of agglomerates \hspace{1cm} [nm]

$D_f$ \hspace{1cm} mass fractal dimension

$d_p$ \hspace{1cm} primary particle diameter \hspace{1cm} [nm]

$d_{ai}, d_{aj}$ \hspace{1cm} particle size of agglomerate i, j \hspace{1cm} [nm]

$n$ \hspace{1cm} aerosol number concentration \hspace{1cm} [#/cm$^3$]

$M_k$ \hspace{1cm} $k^{th}$ moment of aerosol size distribution

$N$ \hspace{1cm} total number concentration \hspace{1cm} [#/cm$^3$]

$N_{pp}$ \hspace{1cm} number of primary particle size \hspace{1cm} [#]

$k_b$ \hspace{1cm} Boltzmann's constant \hspace{1cm} [#/mole]

$T$ \hspace{1cm} temperature \hspace{1cm} [K]

$V_g$ \hspace{1cm} geometric number mean volume

**Greek Letters**

$\beta$ \hspace{1cm} Collision frequency function

$\sigma_g$ \hspace{1cm} Geometric standard deviation

$\sigma_{g_0}$ \hspace{1cm} Initial Geometric standard deviation

$\mu$ \hspace{1cm} Gas viscosity \hspace{1cm} [Pa.s]

$\tau_f$ \hspace{1cm} Self preserving time lag for fractal nanoagglomerates \hspace{1cm} [s]

$\tau_n$ \hspace{1cm} Normalized self preserving time \hspace{1cm} [-]

$\rho$ \hspace{1cm} Particle density \hspace{1cm} [kg/m$^3$]
<table>
<thead>
<tr>
<th>Moment</th>
<th>Continuum regime</th>
<th>Free molecular regime</th>
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<td>$\frac{dM_0}{dt}$</td>
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<td>$\frac{dM_2}{dt}$</td>
<td>$2K[M_1^2 + M_{(D_f+1)/D_f}M_{(D_f-1)/D_f}]$</td>
<td>$2Kb[M_1 M_{2/D_f+1/2} + 2M_{1+1/D_f}M_{1/D_f+1/2} + M_{1+2/D_f}M_{1/2}]$</td>
</tr>
</tbody>
</table>

Table 1: Comparison of $M_0$, $M_1$, and $M_2$ in two different regimes (Park and Lee, 2001)
<table>
<thead>
<tr>
<th>Set</th>
<th>$\sigma_0$</th>
<th>Mass fractal dimension</th>
<th>Particle number concentration(#/cm$^3$)</th>
<th>Primary particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2.0/2.5/3.0</td>
<td>$10^{16}$</td>
<td>1~20</td>
</tr>
<tr>
<td>3</td>
<td>1~3</td>
<td></td>
<td></td>
<td>1~20</td>
</tr>
</tbody>
</table>
Figure 1 Asymptotic $\sigma_g$ as a function of $D_f$
Figure 2 Effect of $d_p$ as a function of $D_f$ on: (a) geometric standard deviation; (b) self preserving time lag.
Figure 3 Effect of mass fractal dimension and primary particle size on $\tau_f$ in the free molecular regime
Figure 4 Comparison of $\tau_f$ to attain the self preserving distribution ($dp = 2$ nm and $D_f = 3$)
Figure 5 Effects of $D_f$ and $\sigma_{g0}$ on the self preserving time lag: (a) $d_p = 2$ nm; (b) $d_p = 20$ nm
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BIOGRAPHICAL SKETCH

Ki-Joon Jeon was born in Seoul, Korea, in 1973 and grew up in Seoul, Korea. He attended the In-ha University in the Environmental Engineering Department. After his sophomore year in the University, he joined the Army and served at the Korean Air Force base. After three years of service in the Army, he continued his studies and received BS and MS degrees in environmental engineering at Inha University, Korea, in 2001. He then decided to pursue Ph.D. degree in the USA. In 2003, he was granted admission to the PhD program at the Department of Environmental Engineering Science at the University of Florida, with an Alumni fellowship from Dr. Chang-Yu Wu to Environmental engineering and Sciences. He received a scholarship from Korean Science & Engineering Foundation (M06-2003-000-10264-0). His research interests include hydrogen storage and nanoparticle synthesis and his current project involves the kinetics of metal hydride formation.