Stability of magnesium based nanoparticles for hydrogen storage

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CHAPTER 4

Improved Thermal Stability of Gas Phase Mg Nanoparticles for Hydrogen Storage

This Chapter describes how to improve the thermal stability of Mg nanoparticles (NPs) for its use in hydrogen storage. Three ways are investigated that can achieve this goal.

(i) Addition of Cu prevents void formation during NP production and reduces the fast evaporation/voiding of Mg during annealing. (ii) Alloying can prevent Mg evaporation: e.g. Mg with Ni forms a thermally stable core/shell (MgNi3/Ni) preventing Mg evaporation during annealing. (iii) Covering Mg NPs with a Ti film leads to suppression of Mg evaporation during vacuum annealing. Indeed, hydrogenation of the Ti/Mg nanoparticles shows formation of the γ-MgH2 phase as noticed for pure Mg nanoparticles.

4.1. INTRODUCTION

Magnesium with its high gravimetric hydrogen storing capacity of 7.6 wt % is considered one of the main candidates for hydrogen storage [1]. Although the improvement in kinetics of hydrogen absorption/desorption has been achieved by ball milling Mg with catalysts and by alloying [2-5], the problem associated with the high enthalpy of formation of the Mg-hydride is still presenting major difficulties. It has driven attention to Mg nanostructures. Nanoparticles and nanowires of Mg above 50 nm do not show any significant improvement in thermodynamics [6,7]. Similarly, nanoconfinement of Mg and Mg-hydride in the porous carbon aerogel scaffold material also did not show any thermodynamic changes [8-10]. On the other hand, the prediction from theoretical calculations shows that the thermodynamics of the Mg-hydride can be improved if the size of the nanoparticles can be reduced to below 2 nm [11,12].

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Therefore a lot of interest has been paid to producing Mg nanoparticles below 5 nm, because a low desorption temperatures compared to bulk Mg has already been reported in this case [13, 14]. However, our recent observations show that a reduction in size will increase the evaporation rate of Mg nanoparticles during annealing in a hydrogen atmosphere [15]; evaporation even results in the formation of a complete hollow Mg core (based on the Kirkendall effect associated with evaporation). The thermal stability of Mg nanoparticles is a serious issue, because the increase of the vapor pressure with decreasing nanoparticle size will always enhance the evaporation of Mg. Similarly, the voids that are formed during production within Mg nanoparticles (due to the oxidation based Kirkendall effect) have also major impact on accelerating the formation of an empty Mg nanoparticle core leaving behind an MgO nanoshell [15].

These observation shows that the void formation and increased Mg evaporation rate with decreasing nanoparticle size represent formidable limitations for using Mg nanoparticles in hydrogen storage [15,16]. In this work, we address these problems and discuss strategies in improving the thermal stability of Mg nanoparticles by preventing voiding. These approaches are based on i) addition of 1/8 Cu to a 7/8 Mg target, ii) alloying Mg with Ni, and iii) and covering Mg nanoparticles with a Ti film. Within this framework, high-resolution transmission electron microscopy (HRTEM) was employed to study the atomic scale structural details of the produced Mg-based nanoparticles in close comparison with studies of pure Mg nanoparticles.

4.2. EXPERIMENTAL PROCEDURE

The Mg-Cu, Mg, Mg-Ni nanoparticles were produced by an Oxford Applied Research NC200U nanoparticle source (www.oaresearch.co.uk.). The sample chamber was evacuated to a base pressure of ~ $1 \times 10^{-8}$ mbar with a partial oxygen pressure of ($\sim 10^{-9}$ mbar) [17,18]. Supersaturated metal vapor is produced by magnetron sputtering of a target consisting of Mg(7/8) and Cu(1/8) for Mg-Cu nanoparticles, Mg$_2$Ni alloy target for Mg-Ni nanoparticles, and pure Mg target for Mg nanoparticles in an inert Krypton atmosphere (pressure of $\sim 0.25$ mbar). All targets were obtained from Alpha Aesar with a purity of 99.99 %. The nanoparticles were transported with a drift gas from the aggregation volume and were deposited on 25 nm thick silicon-nitride membranes, which
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were used for HRTEM imaging and energy dispersive x-ray (EDX) analysis in a JEOL 2010F TEM. *In situ* covering of Mg nanoparticles with a Ti film of ~15 nm thick was performed with a mini e-beam evaporator, directly after the Mg nanoparticles were deposited on Si-nitride membranes for TEM analysis [16,17].

4.3. RESULTS AND DISCUSSION

4.3.1. Influence of Cu addition

During the hydrogenation of Mg nanoparticles at 300 °C, a hollow Mg core was formed (due to the Kirkendall effect associated with Mg evaporation) [15]. Void formation due to metal oxidation is normally known as a Kirkendall effect, because the cation and anion fluxes through the oxide scale are unequal, resulting in a net flow of vacancies, which coalesce into voids below the oxide scale [16]. However, in our case we also associate the Kirkendall effect with evaporation due to the inward diffusion of vacancies (through the oxide) coupled to an outward diffusion of Mg [15]. The evaporation rate shows a size effect: The smaller the nanoparticles the faster they form an empty Mg core [15]. In controlling the evaporation of Mg and voiding, we started with the addition of Cu to Mg. Fig. 4.1 a shows that the produced Mg-Cu nanoparticles with an addition of 1/8 Cu to an 7/8 Mg target prevent the void formation in the Mg core. Indeed, the produced Mg-Cu nanoparticles generally have a Cu-rich (Mg$_2$Cu) part in one of the corners of the Mg core as can be seen from Fig. 4.1 b.

Energy Dispersive X-ray (EDX) analysis of the Mg-Cu nanoparticles confirmed the presence of Cu in the corners of an otherwise pure Mg core. Furthermore, Fourier Transform analyses of the HRTEM images of the Cu rich parts with (interplanar spacing of pure) Mg core as reference enabled us to confirm that the Cu rich area is indeed the Mg$_2$Cu phase. TEM analysis shows that Mg-Cu nanoparticles do not show any hollow faceted voids. These voids were observed in pure Mg nanoparticles at the Mg/MgO interface due to the oxidation [16], since the outward diffusion of Mg is faster in comparison to the inward diffusion of oxygen followed by a fast rearrangement and clustering of vacancies into the voids. The absence of voids in the Mg-Cu nanoparticles can be attributed to the fact that the rate of outward diffusion of the metal (cations) compared to the inward diffusion of oxygen (anions) is reduced. This factor in return
indicates that in the Mg core, e.g., outside the Mg$_2$Cu part, to some extent Cu atoms must have been dissolved in it.

![Figure 4.1](image)

**Figure 4.1** (a) Bright-Field TEM image showing an overview of Mg-Cu nanoparticles produced in the size range 15-70 nm without voids. (b) HRTEM image showing an Mg-Cu nanoparticle with a Cu rich (Mg$_2$Cu) part in one of the corners of Mg core, with a very thin amorphous oxide shell exactly where the Cu rich (Mg$_2$Cu) part is present. In contrast, around the Mg core a crystalline MgO shell is present.

Normally it has been observed that the Mg nanoparticles with voids (upon production) would enhance the rate at which the hollow Mg core is formed. Our previous study
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indicates that the time taken to form an initial void during annealing of the Mg nanoparticles is longer than the void growth and hollowing of the Mg core [15], which shows that the nanoparticles (without initial void formation due to oxidation based Kirkendall effect) will certainly improve the stability of the Mg core as compared with the pure Mg nanoparticles with void. The rate of void formation and growth during annealing decreases with the increase in particle size.

4.3.2. Alloying of Mg with Ni

With the poor thermal stability of Mg nanoparticles during annealing and hydrogenation, it is worth to further investigate the effect of alloying. For this reason we produced Mg-Ni nanoparticles, where we varied the composition of Ni in the Mg-Ni nanoparticle and studied its effect on the thermal stability of Mg. As a matter of fact we can infer from our TEM analysis that Mg-Ni nanoparticles with on average 60:40 at. % composition are indeed stable after in-situ TEM annealing, and in hydrogen atmosphere (under 6 bars pressure) held at 300 °C for 40 hours without any void formation and evaporation. Figure 4.2a shows bright field image of Mg-Ni nanoparticles after in-situ TEM annealing at 300 °C for 7 hours. Note that the composition of individual nanoparticles can show distinct variations with respect to the 60:40 at. % ratio. Furthermore, the Mg-Ni nanoparticles with MgNi2/Ni core shell are also stable under in-situ TEM annealing as it is shown by Fig.4.2 b. However, for hydrogen storage it is necessary that the Mg % is significantly higher in the alloy since it determines the total gravimetric density of hydrogen that can be stored in alloy nanoparticles. Nevertheless, if the Mg content in alloy nanoparticles is increased then also the void formation again develops during annealing of the particles, although the Mg evaporation was not as serious as it was observed for pure Mg nanoparticles. Indeed, we also tried to increase the Mg composition with a section target like (¼ of Ni and ¾ of Mg) but the annealing results shows that even though there was a presence of Ni in the nanoparticles, the evaporation of Mg could not be controlled.
4.3.3. Ti Covering on the Top of Mg nanoparticles

With the prospect of hydrogen storage applications, in order to use pure Mg nanoparticles, since they have the highest hydrogen gravimetric density (7.6 wt % in bulk), we also considered the case of covering Mg nanoparticles with a nanometer thickness (~ 15-20 nm) Ti layer on top. Although a Ti layer can be used for hydrogen dissociation, and as a catalyst for hydrogen absorption and desorption [18,19], here the
**Figure 4.3** (a) Bright-field TEM image of Mg nanoparticles covered with a Ti film (~15 nm thick). (b) Ti covered Mg nanoparticle after annealing in vacuum at 300 °C for 5 hours and at 350°C for 1/2 hour without any Mg evaporation and void formation. (c) Diffraction pattern of the sample after annealing showing the presence of Mg, which remains identical to the diffraction pattern of the sample before annealing.
main motivation was to see the effect of Ti in protecting nanoparticles from Mg evaporation [15].

After annealing in in-situ in TEM at 300 °C for 5 hours, and 350 °C for ½ hour (to gauge the effect of increased temperature), Mg nanoparticles covered with Ti remained almost unchanged as Figs. 4.3 b, c. indicate. Therefore, Mg nanoparticles covered with Ti favor the suppression of Mg evaporation in comparison with Mg bare nanoparticles. Assuming Ti is a perfect diffusion barrier for Mg, the evaporation of Mg in the small enclosed volume quickly establishes the equilibrium pressure and thus the evaporation is stopped. Here the driving force (the difference in actual and equilibrium vapor pressure) for evaporation vanishes. In any case, the hydrogenation of the Mg nanoparticles covered with Ti shows the orthorhombic MgH$_2$ phase along with the TiH$_2$ phase.

We have shown that the evaporation of Mg NPs depends on their specific situation [15]. The effect of alloying Mg is straightforward, because reduces the Mg vapor pressure of the alloy with respect to pure Mg. Since the outward Mg flux is reduced also the inward vacancy flux diminishes, the Kirkendall effect is suppressed. In the case of Ti coverage, the evaporating (pure) Mg NPs quickly attain their vapor pressure in the limited volume enclosed by the Ti layer. When the vapor pressure is reached, no further net evaporation will occur. Also in this case the Kirkendall effect is strongly suppressed.

4.4. CONCLUSION

In this work we placed emphasis on improving the thermal stability of Mg nanoparticles for possible use in hydrogen storage. Indeed, we have shown that addition of Cu can prevent the void formation in the Mg nanoparticles during its production. Alloying Mg with Ni can prevent Mg evaporation, but it depends on the concentration of Ni in the alloy nanoparticles and requires too much Ni. Covering Mg nanoparticles with a Ti film shows a promising sign for the suppression of Mg evaporation and the use of Mg nanoparticles for hydrogen storage.
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