University of Groningen

Influence of Ti on the formation and stability of gas-phase Mg nanoparticles
Krishnan, Gopi; Palasantzas, G.; Kooi, B. J.

Published in:
Applied Physics Letters

DOI:
10.1063/1.3533812

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2010

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
Influence of Ti on the formation and stability of gas-phase Mg nanoparticles

Gopi Krishnan, a) G. Palasantzas, b) and B. J. Kooi a)

Department of Applied Physics, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

(Received 15 September 2010; accepted 14 December 2010; published online 30 December 2010)

The effect of titanium on magnesium nanoparticle formation is investigated in relation to the importance of Mg in hydrogen storage. Addition of Ti reduces the Mg-nanoparticle sizes in the range of 5–20 nm and leads to less protective Mg-oxide shells. This in return accelerates the evaporation of Mg that leads to hollow Mg cores. The presence of oxygen plays a dual role in forming MgO protected stable Mg nanoparticles above a critical size (~15 nm) and hollow ones below this size both due to evaporation and oxidation associated Kirkendall effects. © 2010 American Institute of Physics. [doi:10.1063/1.3533812]

Nanoparticles have been investigated extensively in recent years due to their physical properties indicating high potential for technological applications. They exhibit chemical and physical properties because of size and structure selective quantum confinement or the large surface to volume ratio.1–3 The control of nanoparticle size and stability is an important and challenging issue in the size range below ~5 nm, which is the so called mitoedral region where the pronounced nanosize effects are found especially for catalyst.3,5 Magnesium—a system with a high storage capacity of 7.6 wt % hydrogen1—has attracted strong interest for application in hydrogen storage, also with Mg in the form of nanoparticles. Indeed, theoretical calculations predict improvement of the thermodynamics of MgH2 as the particle size decreases,6 which is necessary for hydrogen release at relatively low temperatures. Therefore a lot of attention has been paid to the preparation of Mg nanoparticles with sizes below 5 nm.7,8

However, Mg has a high affinity to oxygen, leading to oxidation of Mg nanoparticles. Formation of voids upon oxidation, sulfidation, and nitridation is a common phenomenon in nanoparticles, which is conceptually related to the Kirkendall effect.1,9,10 The latter is the result of a faster outward diffusion of metal ions with simultaneous inward diffusion of vacancies to compensate for the unequal material flow due to the different atomic diffusivities.9,10 Notably the Kirkendall effect associated with Mg evaporation has been the cause of voiding of Mg nanoparticles under different annealing conditions, which can take place during hydrogen storage.11

Due to the strong affinity for oxygen, Mg nanoparticles will always form an outer MgO shell, even in an ultrahigh vacuum environment.12 The quality and the density of the MgO shell have major influence on the stability of the Mg nanoparticles, i.e., suppressing evaporation of Mg and the formation of hollow nanoparticles.13 On the other hand the presence of the oxide layer, if it is sufficiently thick, on top of Mg is a barrier for hydrogen diffusion during the hydrogen absorption/desorption.14,15 In this work, we will show how the presence of oxygen can play a major role in the formation and stability of Mg nanoparticles for sizes, especially, in the range of 5–15 nm. For this purpose we added Ti, which also acts as a getter of O, and we compare the results with previous studies of pure Mg nanoparticles.

The Mg nanoparticles with addition of Ti were produced by the nanoparticle source NC200U from Oxford Applied Research (www.oaresearch.co.uk). The sample chamber was evacuated to a base pressure of ~1×10−8 mbar with a partial oxygen pressure of ~1×10−5 mbar.12,16 Supersaturated metal vapor is produced by magnetron sputtering of a sectioned target consisting of 2/3 Mg and 1/3 Ti (99.95% purity of the Mg and Ti is obtained from Alpha Aesar) in an inert krypton atmosphere (pressure ~0.25 mbar). The nanoparticles formed in the aggregation volume are removed fast by the use of helium (He) as a drift gas. The nanoparticles transported from the aggregation volume were deposited onto 25 nm thick silicon-nitride membranes, and further analysis was performed with a JEOL 2010F transmission electron microscope.12,16

Figure 1 shows that—by adding 1/3 Ti to the source Mg target—three types of nanoparticles are produced: (1) with a completely hollow Mg core and only a Mg-oxide shell remaining, (2) with a Ti particle filling a small fraction of a hollow core surrounded by a MgO shell, and (3) with a non-hollow Ti core surrounded by a MgO shell. Examples for these three types of particles are clearly indicated in Fig. 1. Analysis from Fig. 1 confirms that ~55% of the produced nanoparticles, with sizes between 5 and 10 nm, have a completely hollow Mg core. Our motivation for adding Ti was to investigate its effect on the thermal stability of Mg nanoparticles.17 In this respect the formation of hollow Mg cores is interesting. This formation of hollow cores occurs for two reasons. (1) The effect of Ti on oxygen: during the sputtering/production of the nanoparticles the Ti sputtered from the target acts as a getter element for the absorption of oxygen similar to a Ti sublimation pump. In turn this process affects the partial pressure of the oxygen present during the growth of a thin protective Mg-oxide shell and its quality (being not crystalline), which cannot prevent the Mg core from evaporating. (2) Size effect: reduction of the Mg-nanoparticle size having a thin (~1–2 nm) MgO oxide shell is just sufficient for the smaller nanoparticles to evaporate since the reduction of the nanoparticle size increases the vapor pressure $P_0$ of nanoparticles as the Kelvin.
\[ \frac{P_s}{P_{so}} = \exp\left(\frac{4\gamma M}{\rho_p RTd}\right) \] with \( P_{so} \) the vapor pressure of a flat surface—indicates.\(^1\)

This behavior, responsible for the formation of an empty Mg core, is already observed in our previous studies with the annealing of pure Mg nanoparticles\(^1\) which shows a thermodynamic size effect on the evaporation rate of Mg nanoparticles, where the evaporation rate increases as the particle size decreases.\(^1\) In the present study the reduction of Mg-nanoparticle sizes is due to Ti because Ti acts as nucleation centers and increases the number of particles, which subsequently experience less growth. Therefore smaller nanoparticles are formed with a hollow Mg core as comparison with pure Mg nanoparticles shows.

Once the size of the Mg nanoparticles increases above 15 nm, which is possible by increasing the aggregation length of the nanocluster source, these nanoparticles do not become hollow, see Fig. 2. Comparing results from our previous studies\(^1,2\) and Fig. 2, we can infer that the Mg nanoparticles only above a certain critical size (\(\sim 15\) nm) have the hexagonal prismatic shape. Nanoparticles with this shape have a high quality crystalline MgO shell around the Mg core with an orientation relation between them.\(^2\) This crystalline oxide shell of \(\sim 3–4\) nm thick makes the Mg nanoparticles stable and is not observed for sizes below 15 nm.\(^2\) The latter observation indicates that the size, shape, crystallographic quality of the oxide shell, and the MgO/Mg orientation relationship (OR) are important factors that contribute to an improved stability of the Mg nanoparticles above the critical size. Moreover, Mg nanoparticles produced (without Ti) always showed a size distribution from 10 to 80 nm, whereas with addition of Ti, the size of Mg nanoparticles and the width of the distribution have been reduced, as can be clearly seen from Figs. 1 and 2. The effect of Ti as nucleation centers for the growth of Mg-core/MgO-shell nanoparticles can also be seen from these figures. Indeed, the dark contrast of the bright-field image indicates the presence of Ti even after the Mg core is hollowed leaving behind an oxide shell with a Ti particle filling only a small portion of the hollow core.

In Fig. 3, high-resolution transmission electron microscopy (HRTEM) images confirm that the produced nanoparticles have a Ti core or a hollow Mg core with a MgO shell. We also produced nanoparticles from an alloy target with higher content of Ti (Mg 70 wt % and Ti 30 wt %), as it is shown in Fig. 4. The nanoparticles show a size distribution between 3 and 40 nm. Mg nanoparticles below 15 nm in size are hollow as it was observed earlier. Our energy-dispersive x-ray spectroscopy and electron-energy-loss spectroscopy
analysis confirms that there are also Ti nanoparticles present along with those of Mg but they are not hollow. The latter confirms that all the nanoparticles in Fig. 4 with a hollow core or with a void are Mg nanoparticles. Here, also the nanoparticles with sizes below 15 nm, after Ti addition, form thinner oxide shells without OR, which cannot prevent Mg evaporation and formation of a hollow core. For the Mg nanoparticles produced with the pure Mg target, our previous results show that the Mg nanoparticles produced in the size range of 10−15 nm show the formation of a hollow Mg core predominantly due to the Kirkendall effect associated with evaporation and/or oxidation. In contrast, the addition of Ti leads to hollowing due to the Kirkendall effect associated with evaporation. Which type of Kirkendall effect (either based on evaporation or oxidation) plays the dominant role thus depends on the condition inside the aggregation volume. Therefore, it is clear that if we produce Mg nanoparticles without a proper oxide shell, our results predict that they would not be stable against evaporation.

In conclusion, we have investigated the effect of Ti on Mg nanoparticles. Ti reduces the nanoparticle size and evaporation; the latter by influencing the MgO oxide shell. Especially the effect of Ti is dominant for the particle sizes below 10 nm because (i) the MgO oxide shell has less quality and cannot prevent evaporation and (ii) smaller nanoparticles anyhow have higher vapor pressure and are thus more prone to evaporation. Finally, we have shown that the condition (particularly oxygen partial pressure) inside the aggregation volume plays a major role in the formation of hollow Mg cores below a critical size of 15 nm based on the Kirkendall effects associated with evaporation and/or oxidation.

We would like to thank Zernike Institute for Advanced Materials for financial support of this work.

11G. Krishnan, B. J. Kooi, G. Palasantzas, Y. Pivak, and B. Dam, J. Appl. Phys. 107, 053504 (2010). The other parameters in the Kelvin equation are defined as follows: γ is the surface energy, M is the molecular weight, ρ is the density of the particle, R is the gas constant, and T is the temperature; W. Thomson, Philos. Mag. 42, 448 (1871); K. K. Nanda, F. E. Kruis, and H. Fissan, Phys. Rev. Lett. 89, 256103 (2002).