This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Synthesis and exceptional thermal stability of Mg-based bimetallic nanoparticles during hydrogenation.

Gopi Krishnan, a Raluca F. Negrea, b Corneliu Ghica, b Gert H. ten Brink, a Bart J. Kooi, a and George Palasantzas, a

a Zernike Institute for Advanced Materials and the Materials Innovation Institute, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.

b National Institute for Materials Physics, P.O. Box MG-7, Magurele, Ilfov, RO 77125, Romania

KEYWORDS: Mg-based bimetallic nanoparticles, Phase segregation, thermal stability, Gas phase synthesis, hydrogen storage, Nano alloying, core-shell nanoparticles.

Corresponding Author
Email: gopi.k.krish@gmail.com

Abstract

Here we report an extraordinary thermal stability of Mg rich bimetallic nanoparticles (NPs), which are important for hydrogen storage technology. The enhanced NP stability is accomplished because of two critical improvements: (i) No void development within NPs (nanoscale Kirkendall effect) during their formation; (ii) Suppressed Mg evaporation and NP
hollowing during Mg hydrogenation at elevated temperature. The mechanism leading to the improved thermal stability of Mg-based bimetallic NPs is shown to be due to MgH$_2$ hydride formation before evaporation can take place. These findings were tested for various compositions of Mg with Ni, Cu, and Ti, which are interesting combinations of materials for hydrogen storage systems. To achieve this we first demonstrate the synthesis mechanism of Mg-Ni and Mg-Cu NPs, which are well controlled at the single particle level, in order to accomplish multi-shell, alloy and intermetallic structures of interest for hydrogen storage tests. Aberration corrected transmission electron microscopy was carried out to unravel the detailed atomic structure and composition of the bimetallic NPs after production, processing, and hydrogenation. Finally, a simple and effective methodology is proposed for tuning the composition of the Mg-based bimetallic NPs based on the temperature-dependent nucleation behavior of NPs in the gas-phase.

**Introduction**

Magnesium (Mg) with its light weight and 7.6 wt % of H storage capacity is considered as one of the potential candidates for hydrogen storage.$^1$ The slow kinetics for hydrogen absorption/desorption, and the high thermodynamic stability arising from the negative (low) enthalpy of MgH$_2$ formation have been the motivation behind the considerable attention that is paid to Mg nanoparticles (NPs). Although the decrease in Mg NP size (<2 nm) is considered as a favorable forward step towards reducing the formation enthalpy of MgH$_2$, the size reduction below 20 nm turned out to have formidable consequences for Mg NPs. For example in $^{3-5}$ it was found that the high vapor pressure of smaller Mg NPs (<20 nm) leads to higher evaporation rates of Mg than for bigger NPs (>20 nm), where they evaporate much faster during hydrogenation at
temperatures above room temperature. In\textsuperscript{5} it was demonstrated that void formation occurs for NPs larger than 10 nm, and that hollow MgO NPs are formed for NPs less than 10 nm due to oxidation induced nanoscale Kirkendall effect during NP production.\textsuperscript{3} The latter is the result of faster outward diffusion of Mg ions with simultaneous inward diffusion of vacancies to compensate for the unequal material flow due to the different atomic diffusivities. Furthermore, the vacancies supersaturate to form voids within the NPs. As a result smaller Mg NPs (<10 nm) completely transform into hollow NPs, and the bigger NPs (>10 nm) develop voids in the vicinity of their facets within the nanoparticles and these voids grow further during hydrogenation.\textsuperscript{3} Although these phenomena present formidable barriers for the successful implementation of Mg NPs in hydrogen storage, the use of Mg bimetallic NPs might alleviate the issues above.

Indeed, bimetallic NPs are considered as an interesting class of materials, where the chemical and physical properties can be tailored based on composition, size, and atomic ordering. In fact, Mg-based bimetallic NPs produced up to date are mostly based on bottom up methods consisting of inert-gas condensation,\textsuperscript{6} spark discharge generation,\textsuperscript{7} and the hydrogen plasma-metal reaction/arc method.\textsuperscript{8,9} However, none of these methods have shown a well-controlled tuning of sizes, structural motifs, and composition of bimetallic NPs. In addition, although the gas-phase synthesis of NPs via DC-magnetron sputtering is well known to produce metallic and bimetallic NPs, only recently the capability of this technique to control different bimetallic structures was demonstrated.\textsuperscript{10,11} In fact, we demonstrated a general methodology to tune various structures of, bulk immiscible, bimetallic NPs at the single particle level using our home modified Mantis nanocluster source.\textsuperscript{10}
Bimetallic Mg-rich based NPs combined with other metals like Ni, Cu and Ti, which are interesting as hydrogen storage materials,¹ are highly challenging to synthesize using gas-phase synthesis with controlled composition and structure. This can be attributed to the different physical properties (e.g. vapor pressure and melting point) of Mg and the combined elements (e.g. Ni, Cu and Ti), which affect the size, nucleation, and the composition of the bimetallic NPs. These factors demand change of sputtering target composition in order to alter the NP chemical composition. Here, however, we will demonstrate that it is feasible to achieve composition tuning of Mg-Ni, Mg-Cu, and Mg-Ti NPs based on a temperature dependent nucleation behavior of Mg, Ni, and Cu using only a single composition (sectioned) material target for magnetron sputtering and gas phase synthesis of NPs. To the best of our knowledge, tuning different structures of Mg-based bimetallic NPs, tailoring composition during production, and thermal stability have not been reported before.

Hence in this letter we demonstrate: (i) the complete suppression of voids during the synthesis of Mg-Ni, Mg-Cu, and Mg-Ti NPs with Mg rich composition, (ii) improved thermal stability of Mg-(Ni, Cu, Ti) without the formation of a hollow Mg core during hydrogenation of NPs at 250 °C and 10 bar pressure of H₂, and (iii) a synthesis methodology to tailor the composition and different structures of Mg-based bimetallic NPs at single particle level, where proof for the different structures comes from aberration corrected transmission electron microscopy. Finally this paper is dedicated only to the synthesis and in depth characterization of Mg based bimetallic nanoparticles, as well as their thermal stability during hydrogenation.

**Experimental Methods:**

**Synthesis.** The Mg-Ni, Mg-Cu and Mg-Ti bimetallic nanoparticles with various structures (alloys, multishell and multiphase) and composition were produced by a home modified
nanoparticle system Nanosys500 from Mantis Deposition Ltd. (www.mantisdeposition.com). The sample chamber was evacuated to a base pressure of ~1x10^{-8} mbar with an oxygen partial pressure of (~10^{-11} mbar). Supersaturated metal vapor is produced by magnetron sputtering of a sectioned target shown (99.95% purity of the Mg, Ni, Cu and Ti as obtained from Alpha Aesar) in Figure 1 (a) or (b) in an inert Argon atmosphere (pressure of ~0.25 mbar with an appropriate discharge current depending on the choice of the structures that were synthesized). The supersaturated metal vapor is then cooled by argon gas in order to form nuclei, which can subsequently grow into nanoparticles. The nanoparticles formed in the aggregation volume are removed fast by the use of argon which act as a drift and sputter gas. The tuning of the thermal environment and energy was made by varying the discharge current and by keeping the pressure constant inside the aggregation volume.

**TEM analysis:** The nanoparticles transported from the aggregation volume were deposited onto 25 nm thick silicon-nitride membranes, which were used for Transmission Electron Microscopy (TEM) analysis in a JEOL 2010F and JEOL ARM 200F aberration corrected TEM. The TEM investigations performed on a JEM ARM 200F electron microscope is provided with a probe Cs corrector and a Quantum SE Gatan Image Filter. The microscope has been operated at 200 kV acceleration voltage. For the EELS spectrum images we used a convergence semiangle of 20 mrad and a collection semiangle of 49 mrad for a camera length of 3 cm. In order to create a composition line profile across the nanoparticles, an EEL spectrum has been extracted from each pixel along the diameter of the nanoparticle. Each extracted spectrum has been quantified using the Hartree-Slater model for the differential cross-section calculation and the power-law for the background model.
Results and Discussion

Figure 1(a) and 1(b) show bright-field TEM images of Mg-Ni nanoparticles before and after hydrogenation. The NPs show no void formation during their production and no Mg evaporation after hydrogenation at 250 °C (under 10 bar H₂ pressure for 72 hrs). Therefore the present bimetallic NPs show a greatly improved thermal stability as compared to monometallic Mg NPs.³ The compositions of the Mg-rich NPs were 80±3 at% Mg and 20±3 at% Ni (measured using STEM-EELS analysis) with the as-prepared NP structure being solid solution. Our previous analysis has proven that Mg NPs can evaporate and form hollow Mg very rapidly at this temperature and H₂ pressure.³ Moreover, also bimetallic Mg-Cu and Mg-Ti NPs with similar compositions were tested for improved stability, as is shown in the bright-field TEM images of Figure 1 (d, e, g, h).

Although the MgH₂ formation can be achieved at lower H₂ pressure and time, our motivation for prolonged exposure is to observe their long term thermal stability in comparison with monometallic Mg NPs. The diffraction patterns of Figures 1 (c, f, i) confirm that the corresponding NPs are fully hydrogenated having α-MgH₂ rutile phase (see Figure 3(b) HRTEM image in the supplementary information). After hydrogenation, Mg-Ni and Mg-Cu NPs show segregation and phase separation of Ni and Cu to the center of (most of) the NPs that are shown in Figure 1(compare b with a and e with d). This segregation phenomenon can be attributed to the following systematic reasons: (1) Lower enthalpy of MgH₂ formation (-37 kJ/mol H), as compared to Ni (4.5 kJ/mol H) and Cu (24 kJ/mol H), which acts as a driving force for segregation; (2) Enhanced atomic mobility of atoms under the influence of absorbed hydrogen in the NPs, as observed in bulk materials;¹²-¹⁴ (3) Surface energy difference between MgH₂ and Ni (or Cu) drives Mg atoms to the surface to form an MgH₂ shell, and simultaneously Ni (or Cu)
atoms are pushed to the center where they finally form a Ni (or Cu) core (see Figure 3 (a) HAADF-STEM image in the supplementary information).

Our initial observations indicate that phase separation does not take place when Mg-Ni NPs are annealed at 250 °C in vacuum, indicating the clear influence of hydrogen on phase separation. In contrast, phase separation upon hydrogenation (as observed for Mg-Ni and Mg-Cu NPs) does not occur for Mg-Ti NPs indicating their unique behavior as it is shown in Figure 1h. However, the lower enthalpy of TiH$_2$ formation (-72 kJ/mol H) as compared to MgH$_2$ (-37 kJ/mol H), indicates that hydrogen should in general still favor phase separation. Moreover, in the case of Mg-Ti thin films phase separation was not observed also after hydrogenation at low temperature and pressure.$^{15,16}$ The coherent structure and equal molar volume of the TiH$_2$, Mg and influence of hydrogen on the stabilization of Mg-Ti alloys by reducing the enthalpy of formation from positive to negative (Mg and Ti are immiscible systems with a positive enthalpy of formation) are two reasons considered to inhibit phase segregation in thin films.$^{15,16}$ Nevertheless, a full understanding is still missing. Our detailed study to improve the understanding of this behavior for Mg-Ti NPs will be reported elsewhere. In any case enhanced thermal stability of bimetallic Mg NPs is preserved for an Mg concentration of less than < 85 at %, which is valid for Ni, Cu and Ti. Above this Mg concentration void formation and voiding of Mg cores slowly starts to develop during synthesis and hydrogenation depending on the NP size where it is of course more pronounced for smaller NPs (see Figure 4 in supplementary information).

The suppression of void formation in Mg-based bimetallic NPs during their production can be explained qualitatively by three important factors: (1) The presence of Ni, Cu and Ti at the interface of the metal/metal-oxide (Mg/MgO) suppresses vacancy supersaturation and thereby block the coalescence of vacancies to form voids or reduces initial nucleating sites for void
formation and subsequent growth; (2) Presence of vacancy sinks in bimetallic Mg NPs near the metal/metal-oxide interface for vacancy annihilation; (3) Outward diffusion of Mg is slowed during the process of hydrogenation by the formation of intermetallic/alloy near the interface. Indeed, a similar kind of strategy has been employed in thin films of two metals separated with an intermediate alloy layer (made of a combination of the same metals), which efficiently inhibits the void formation due to their reduced atomic diffusivity.\textsuperscript{17,18}

More important is the fact that the Mg-based bimetallic NPs also show an increased thermal stability \textit{during hydrogenation} as compared to pure Mg nanoparticles. This can be attributed to the solid solution (alloy) structure of Mg-based bimetallic NPs, which significantly lowers the Mg vapor pressure as compared to monometallic NPs. The latter can be understood by the fact that the added metals (Ni, Cu, and Ti) have higher melting and boiling points than Mg (in general high boiling point metals have low vapor pressure). For example, Ni has (compared to Mg) low vapor pressure and high thermal stability at all relevant temperatures. Therefore, Mg-based bimetallic NPs with alloy structure should show better thermal stability than Mg. This is confirmed here for Mg-Ni, Mg-Cu and Mg-Ti bimetallic NPs with Mg-rich composition.

During hydrogenation the segregation and phase separation do not lead to void formation within NPs. This can be the effect of stable MgH\textsubscript{2} formation during phase separation of Ni, as the MgH\textsubscript{2} is thermally more stable than Mg, which prevents hollowing of Mg and increases the thermal stability of NPs. In the case of monometallic Mg NPs we observed that the Mg evaporation takes place rapidly before formation of the MgH\textsubscript{2} phase occurs due to its high vapor pressure. Therefore, in the case of Mg-based bimetallic NPs the enhanced stability arises from: (a) the lower vapor pressure of Mg due to alloy structure, which retards the Mg evaporation, and
(b) subsequently allowed formation of MgH$_2$, which further clearly enhances the thermal stability of the Mg-based NPs.

To support this claim we demonstrate that Mg-Ni NPs, with an initial multi-shell structure as shown in Figure 3 (a), when they undergo hydrogenation at two different conditions (250 °C at 10 bar H$_2$, and 150 °C at 5 bar H$_2$) give two different outcomes. First, the Mg-Ni NPs at 250 °C and 10 bar H$_2$ show phase separation, similar as observed in Figure 1 (a), while in the second case, at 150 °C and 5 bar H$_2$, the NPs do not show any phase separation and MgH$_2$ formation. Moreover, the latter NPs only show the presence of an MgO shell and complete absence of Mg in the core of the NP. Ni of course remains, which also suggests that when Mg is not hydrided sufficiently fast it can still easily evaporate (Figure 5 in supplementary information).

In order to be able to control this void formation (nanoscale Kirkendall effect) and thermal stability of Mg rich bimetallic NPs we have developed a synthesis methodology to tune the composition and structure of the Mg-based bimetallic NPs, where for Mg-Ni and Mg-Cu three categories can be distinguished: multi-shell/onion structures, intermetallic compounds, and (solid-solution) alloy structures. The nucleation and growth of the bimetallic NPs was controlled via regulation of the discharge current applied to the material target for DC magnetron sputtering, which is one of the possible paths to control the NPs structures formed during high pressure gas-phase condensation.$^{10,19}$ Indeed, regulation of the discharge current gives a direct control over the thermal environment the NPs experience during their formation, since it allows tuning of the density of the plasma and thus the energy of the sputtering Ar ions and growing NPs. As a result, this process allows tuning of different temperature regimes (as the discharge current increases the plasma temperature also increases at constant gas flow condition) and cooling rates for the NPs during their formation.$^{10}$ The temperature/thermal environment affects
strongly the NP nuclei formation, and their nucleation rate, which is strongly element specific at
different discharge currents. Effectively we can thus use this dependence to tune the structure
and composition of the bimetallic NPs.

In general during binary element thin film formation the elements with high vapor pressure (at
the synthesis condition) will share higher percentages of the composition in the final structure.
However, in bimetallic NPs, e.g. Mg-Ni, the high vapor pressure element (Mg) does not
dominate the final composition of the NPs but rather it depends on the rate of nuclei formation of
Ni (high melting point element) and subsequent growth (and intermixing) of both Mg and Ni.
This is especially valid when the combined elements have large differences in their physical
properties (e.g. vapor pressure and melting points). From our previous observations, a metal with
higher melting point (higher solidification temperature) will always tend to be enriched in the
NPs compared to the accompanying metal in the binary system. Figure 2(a) shows a schematic
of the bimetallic NP formation at different discharge currents at constant flow rate, while Figure
2(b) shows a schematic of the temperature profile the NPs experience at different discharge
currents.

Furthermore, Figure 3(a) shows a bright-field TEM image of Mg-Ni nanoparticles synthesized
at 0.250 A discharge current showing a multi-shell structure (i.e. as opposed to the alloy structure
shown in Figure 1(a)), which can be confirmed from the observed variations in contrast. Figure
3(c) shows a STEM-EELS spectrum mapping of a corresponding NP, which reveals the multi-
shell structure. The NP shows a Ni-core with towards the outside a sequence of Mg rich/Ni/MgO
shells as indicated in the figure, where particularly the intermediate Ni shell is relatively thin.
Figure 3(b) shows a HRTEM image of the NPs indicating the Ni (111) lattice planes, which
confirms the presence of Ni as core. To understand more in detail the composition of Mg and Ni,
we present in Figure 4 (a) and (b) a line profile of the NP composition from the STEM–EELS spectrum. The composition distribution in a single NP can be clearly seen along with the Ni and Mg rich regions confirming the presence of the multi-shell structure.

In order to understand this multi-shell structure formation, we schematically illustrate this process for Mg-Ni NP in Figure 4 (c), and show how oxidation plays a central role. Unlike most other metals, Mg NPs form an oxide shell during their production, even in ultra-high vacuum systems, due to the very high affinity of Mg for oxygen. As shown in Figure 4 (c), the particle produced initially will have a core-shell structure with Ni as a core, and an Mg-rich region as a shell. During oxidation Mg atoms diffuse to the surface while the Ni atoms in the Mg-rich shell are pushed backwards as Mg has higher affinity for oxygen to form MgO (ΔH=-601 kJ/mol) rather than Ni to form NiO (ΔH=-239 kJ/mol). Moreover, the surface energy of MgO is lower than Ni, γMgO < γMg < γNi, which also favors the MgO to be an outer shell. Finally this leads to an outer MgO shell followed by a subsurface Ni shell. This process stops once the Mg forms an MgO oxide of certain thickness because the electron transfer (tunneling) mechanism from the metal-oxide interface to the outer oxide surface, necessary for oxidation to occur, decreases exponentially at room temperature when the thickness of the oxide shell increases linearly. Remarkably, this process thus enables the formation of a multi-shell structure within a single NP.

Figure 5 (a) shows a bright field TEM image of Mg-Ni NP produced with higher discharge current of 0.400 A, and Figure 5 (b) shows a corresponding HRTEM image demonstrating the presence of the intermetallic MgNi2 compound (in a mixed state) with a clearly increased Ni at.% than that produced in Figure 3 (∼73 versus ∼42 at.% Ni). Similarly, an intermediate current 0.350A also shows a solid solution in the Mg-Ni NPs but with a Ni concentration at an intermediate level (∼60 at.% Ni) between those obtained with 0.250 and 0.400 A discharge
currents. The latter confirms the fact that at higher discharge current the temperature profile that these NPs undergo is in general higher allowing the formation of a solid solution/intermetallic structure more enriched in the higher melting point element. However, for hydrogen storage applications we need Mg-rich particles as increase in Ni concentration would not only increase the overall weight of the material but simultaneously the hydrogen storage capacity is reduced. Therefore, instead of using half section targets of Mg and Ni, we adopted a section target of \( \frac{3}{4} \) Mg and \( \frac{1}{4} \) Ni. As a result the Mg-Ni NPs produced at 0.250 A show an increased Mg concentration of 80 at.% in solid solution, which is in fact the result shown in Figure 1 (a – c). With a discharge current of 0.350 A an intermetallic \( \text{Mg}_{2}\text{Ni} \) compound is formed consisting of 70 at.% Mg as shown in Figure 5(c) & (d). The latter results again confirm the fact that at higher discharge current the (high vapor pressure) Mg concentration reduces against that of the high melting point element Ni.

In order to see now the evolution of Mg-Cu NPs with a similar strategy as for the Mg-Ni system, we selected a section target of \( \frac{1}{2} \) Mg and \( \frac{1}{2} \) Cu. Figure 6 (a) shows a HAADF-STEM image and Figure 6 (b) a bright field TEM image of the Mg-Cu NPs produced at 0.250 A. In comparison with Mg-Ni at the same conditions, the Mg-Cu NPs also display a similar kind of structure. However, a detailed compositional line profile analysis of the NPs from STEM–EELS shows a variation of the Cu composition from the center to the outer surface of the NP as it is shown in Figure 6(c) and 6 (d). These profiles clearly show, unlike Ni, that Cu does not have a pure core and multiple shell structure but it rather forms a multiphase region from the center to outer surface of the particles. The Mg-Cu NPs structure consists of a core region, which is a solid solution rich in Cu as it is verified from HRTEM and HRSTEM images (see Figure 6 in supporting information). This is followed by an Mg rich solid solution region, a very thin Cu...
shell, and an MgO shell at the outer surface. Similar to the Ni case, Cu is also present at the subsurface as a shell before the MgO layer, as it can be seen in HAADF-STEM images of Figure 6 (a). Once the discharge current is increased further to 0.350, it forms an Mg$_2$Cu intermetallic. This is shown in Figure 6 (e) and the corresponding HRTEM image of Figure 6 (f), which displays the lattice spacing of the Mg$_2$Cu (040) planes. Finally, as the discharge current is increased further to 0.400 A, the NPs form a solid solution, Figure 6 (g), with compared to Mg$_2$Cu a further increase in Cu concentration.

If we compare now the Ni and Cu concentrations in Mg-Ni and Mg-Cu NPs produced at the same conditions, Figure 6 (h), it is evident that the Ni concentration is more than twice the one of Cu. When the discharge current is increased the increase in concentration of Ni is also more pronounced than that of Cu. This can be attributed to differences in the rate of nuclei formation and their growth at that particular condition. To understand the formation of Mg-Ni and Mg-Cu NPs we have to understand the solidification of Mg-Ni and Mg-Cu. From the Mg-Ni equilibrium phase diagram, Ni will solidify first because it has a higher melting point of 1455 °C as compared to that of Mg of 650 °C. In an atomic vapor of Mg-Ni, Ni will solidify first and form nuclei and then Mg will start to solidify on Ni, because it is relatively easy for Mg to grow on Ni. This is also supported by our experimental observation that we do not see any separate pure Mg and Ni NPs. According to our previous observation on Mg NPs, Mg always tends to have a difficulty in homogenous nucleation, and it would require some species of impurity to nucleate. At 0.250 A (Plasma temperature ($T_p$)= 2.0 x 10$^6$ K) discharge current, Mg is able to grow relatively easy, as the thermal environment and gas temperature are relatively moderate and thus favorable for Mg growth. As the discharge current is increased further to 0.350 ($T_p$=2.6 x 10$^6$ K) or 0.400 ($T_p$=3.0 x 10$^6$ K) A (at constant gas flow), the temperature of the plasma is increased.
and the thermal environment the NPs experience is also changed favoring the formation of single alloy/solid solution NPs. Since Mg has relatively low solidification temperature it is not able to grow as easy in the 0.400 A plasma as it was in the 0.250 A one. These differences in nucleation and growth condition for increasing discharge current thus favor a Ni-rich composition.

In the case of Mg-Cu, Cu solidifies and forms nuclei first and afterwards Mg grows on them, but the main difference with Ni is that Cu has (1) a clearly lower melting point than Ni (1085 °C versus 1455 °C) and thus nucleates at temperatures more close to the solidification temperature of Mg (650 °C) and (2) has still better atomic mobility at these conditions than Ni and forms multi-phase structures instead of a multi-shell structure that is observed in Mg-Ni NPs. Note that the phase diagram of both Mg-Cu and Mg-Ni are rather similar. Similar to Mg-Ni, Mg-Cu also forms single alloy/solid solution structured NPs at 0.350 and 0.400 A discharge currents, however the Cu concentrations in the NPs are observed clearly lower than the Ni ones (and the Mg concentrations thus higher, cf. Figure 6 (h)). This can be attributed to the lower melting point temperature difference between Cu and Mg than between Ni and Mg. Similar behavior is also observed in the case of Mo-Cu, which has higher Mo concentration than Cu at high discharge current of 0.550 A (Mo has a melting point of 2623 °C). In addition, the NPs produced from a 3/4Mg-1/4Cu section target show a lower concentration of Cu as compared to that of Ni, produced at exactly the same condition, as it is shown in Figure 5 (c).

At higher discharge current, the cooling process is effectively reduced due to high temperature (kinetic energy) of the Ar gas molecules that act as a source for energy drain and nuclei formation. Since Cu has a high-energy transfer function and lower bond energy, its nucleation rate is diminished yielding a reduced Cu concentration within NPs. In case of Mg-Ti we also observe the concentration of Ti to increase at higher discharge current, i.e. similar behavior as
observed for Ni and Cu in the Mg-Ni and Mg-Cu. However, we do not observe a multi-shell or multiphase structure as in Mg-Ni and Mg-Cu, which reveals the important point that Mg is not able to dissolve in Ti at 0.250 A discharge current (Mg and Ti are immiscible) and pure Mg develops on top of a pure Ti core during NP formation. As a result no Ti subsurface shell is observed (see Figure 7 in supplementary information). This also proves the oxidation mechanism of Mg-Ni and Mg-Cu produced at 0.250 A discharge current, where subsurface Ni and Cu is accumulated due to the displacement of Ni and Cu backwards within the NP. In Mg-Ti it is always pure Mg that surrounds Ti (no Mg rich area is present), which then logically implies that during oxidation subsurface Ti cannot develop.

**Conclusion**

We have demonstrated the synthesis of bimetallic Mg-based NPs (Mg-Ni, Mg-Cu, and Mg-Ti) with exceptional thermal stability during both their production and hydrogenation, where no void formation takes place. This exceptional thermal stability arises from (1) the addition of high melting point metals (Ni, Cu, and Ti) to Mg in a kind of solid solution and (2) the formation of the hydride MgH$_2$ before Mg evaporates. This stability is maintained for high Mg concentrations in the NPs up to 85 at.%. We also demonstrated a synthesis methodology for tuning the structure and composition of Mg-based bimetallic NPs, which are of interest for high capacity hydrogen storage systems with enhanced surface to volume ratio architectures. Proof for the different NP structures synthesized has been provided by aberration-corrected TEM at the atomic and nanoscale level.
ACKNOWLEDGMENTS

We would like to acknowledge support for this work by The Netherlands Institute of Fundamentals Research for Materials (FOM). RFN and CG acknowledge the financial support of UEFISCDI through the PN-II-ID-PCE-2012-4-0362 project.

Electronic Supplementary Information.

Experimental details including target arrangement, schematic of the gas phase synthesis set up, and TEM images of Mg-Ni, Mg-Cu and Mg-Ni NPs are available. See DOI: 10.1039/b000000x
References


Figure Captions

**Figure 1.** TEM results for Mg-Ni (a-c), Mg-Cu (d-f) and Mg-Ti (g-i) NPs before and after hydrogenation without void formation. (a,d,g) show bright-field TEM images of Mg-Ni NPs with 80±3 at % of Mg, Mg-Cu NPs with 81±3 at % of Mg and Mg-Ti NPs with 85±4 at % of Mg before hydrogenation. (b,e,h) show bright field TEM images of Mg-Ni, Mg-Cu and Mg-Ti NPs after hydrogenation at 250 °C and 10 bar H₂. Mg-Ni and Mg-Cu NPs exhibit phase separation of Ni and Cu (center), and MgH₂ on the outer shell. The Mg-Ti NPs do not show any phase separation. (c,f,i) show a diffraction patterns of the Mg-Ni, Mg-Cu and Mg-Ti NPs after hydrogenation with a clear indication of the rutile MgH₂ formation in all cases.

**Figure 2.** (a) Schematic illustration of the Mg-based bimetallic NP formation at various discharge currents. (b) Effect of discharge current on the temperature profile and cooling rate of the NPs.

**Figure 3.** Bright-field TEM images of the Mg-Ni NPs produced at 0.250 A discharge current. (b) HRTEM Image of the Mg-Ni NP showing a Ni core in which the (111) planes are resolved. (c) STEM-EELS mapping of the Mg-Ni NP.

**Figure 4.** (a) HAADF-STEM image of an Mg-Ni NP. (b) Composition line profile of the Mg-Ni NP from STEM-EELS, from spectrum 1 to 25 as shown in Figure 4 (a) in red. (c) Schematic illustration of the multi-shell structure formation during oxidation of Mg-Ni NPs synthesized at 0.250 A discharge current.

**Figure 5.** (a) Bright-field TEM image of the Mg-Ni NPs produced at 0.400 A (½Mg + ½Ni section target). (b) HRTEM image of the intermetallic MgNi₂ structure. (c) Bright-field TEM
image of the Mg-Ni NP produced at 0.350 A discharge current with $\frac{3}{4}$Mg + $\frac{1}{4}$Ni section target. (d) HRTEM image of the intermetallic Mg$_2$Ni.

**Figure 6** (a) HAADF-STEM image of the Mg-Cu NPs synthesized at 0.250 A. (b) Bright field TEM image of the same Mg-Cu NPs. (c) HAADF-STEM image of an NP synthesized at 0.250 A discharge current, whose composition line profile is shown in Figure (d). (d) Composition line profile of the NP from spectrum 1 to 24 as shown in Figure (c). (e) Bright field TEM image of the Mg-Cu NPs synthesized at 0.350 A with an intermetallic Mg$_2$Cu structure. (f) HRTEM image of the intermetallic Mg$_2$Cu structure. (g) HAADF-STEM image of Mg-Cu NPs synthesized at 0.400 A with a solid solution (alloy) structure, where the Cu composition is higher than the Mg-Cu NPs shown in Figure (a) and (e). (h) Variation of Ni and Cu concentrations in the Mg-Ni and Mg-Cu NPs produced at different discharge currents for $\frac{1}{2}$Mg + $\frac{1}{2}$Ni section targets.
Figure 1. TEM results for Mg-Ni (a-c), Mg-Cu (d-f) and Mg-Ti (g-i) NPs before and after hydrogenation without void formation. (a,d,g) show bright-field TEM images of Mg-Ni NPs with 80±3 at% of Mg, Mg-Cu NPs with 81±3 at% of Mg and Mg-Ti NPs with 85±4 at% of Mg before hydrogenation. (b,e,h) show bright-field TEM images of Mg-Ni, Mg-Cu and Mg-Ti NPs after hydrogenation at 250 °C and 10 bar H₂. Mg-Ni and Mg-Cu NPs exhibit phase separation of Ni and Cu (center), and MgH₂ on the outer shell. The Mg-Ti NPs do not show any phase separation. (c,f,i) show diffraction patterns of the Mg-Ni, Mg-Cu and Mg-Ti NPs after hydrogenation with a clear indication of the rutile MgH₂ formation in all cases. 

160x139mm (300 x 300 DPI)
Figure 2. (a) Schematic illustration of the Mg-based bimetallic NP formation at various discharge currents. (b) Effect of discharge current on the temperature profile and cooling rate of the NPs.
Figure 3. Bright-field TEM images of the Mg-Ni NPs produced at 0.250 A discharge current. (b) HRTEM Image of the Mg-Ni NP showing a Ni core in which the (111) planes are resolved. (c) STEM-EELS mapping of the Mg-Ni NP.

160x129mm (300 x 300 DPI)
Figure 4. (a) HAADF-STEM image of an Mg-Ni NP. (b) Composition line profile of the Mg-Ni NP from STEM-EELS, from spectrum 1 to 25 as shown in Figure 4 (a) in red. (c) Schematic illustration of the multi-shell structure formation during oxidation of Mg-Ni NPs synthesized at 0.250 A discharge current. 

160x118mm (300 x 300 DPI)
Figure 5. (a) Bright-field TEM image of the Mg-Ni NPs produced at 0.400 A (½Mg + ½Ni section target). (b) HRTEM image of the intermetallic MgNi₂ structure. (c) Bright-field TEM image of the Mg-Ni NP produced at 0.350 A discharge current with 3/4Mg + 1/4Ni section target. (d) HRTEM image of the intermetallic Mg₂Ni.

115x103mm (300 x 300 DPI)
Figure 6 (a) HAADF-STEM image of the Mg-Cu NPs synthesized at 0.250 A, (b) Bright field TEM image of the same Mg-Cu NPs, (c) HAADF-STEM image of an NP synthesized at 0.250 A discharge current, whose composition line profile is shown in Figure (d), (d) Composition line profile of the NP from spectrum 1 to 24 as shown in Figure (c), (e) Bright field TEM image of the Mg-Cu NPs synthesized at 0.350 A with an intermetallic Mg2Cu structure, (f) HRTEM image of the intermetallic Mg2Cu structure, (g) HAADF-STEM image of Mg-Cu NPs synthesized at 0.400 A with a solid solution (alloy) structure, where the Cu composition is higher than the Mg-Cu NPs shown in Figure (a) and (e), (h) Variation of Ni and Cu concentrations in the Mg-Ni and Mg-Cu NPs produced at different discharge currents for ½Mg + ½Ni section targets.