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Shape and structural motifs control of MgTi bimetallic nanoparticles using hydrogen and methane as trace impurities†

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In this work we report the influence of methane/hydrogen on the nucleation and formation of MgTi bimetallic nanoparticles (NPs) prepared by gas phase synthesis. We show that a diverse variety of structural motifs can be obtained from MgTi alloy, $\text{TiC}_x/\text{Mg}/\text{MgO}$, TiC_x/MgO and TiH_x/MgO core/shell NPs via synthesis using CH_4/H_2 as a trace gas, and with good control of the final NP morphology and size distribution. Moreover, depending on the concentration of Ti and type of employed trace gas, the as prepared MgTi NPs can be tuned from truncated hexagonal pyramid to triangular and hexagonal platelet shapes. The shape of MgTi NPs is identified using detailed analysis from selected area electron diffraction (SAED) patterns and tomography (3D reconstruction based on a tilt series of Bright-Field transmission electron microscopy (TEM) micrographs). We observe the truncated hexagonal pyramid as a shape of MgTi alloy NPs in contrast to Mg NPs that show a hexagonal prismatic shape. Moreover, based on our experimental observations and generic geometrical model analysis, we also prove that the formation of the various structural motifs is based on a sequential growth mechanism instead of phase separation. One of the prime reasons for such mechanism is based on the inadequacy of Mg to nucleate without template in the synthesis condition. In addition, the shape of the $\text{TiC}_x/\text{TiH}_x$ core, and the concentration of Mg have strong influence on the shape evolution of TiC_x/MgO and TiH_x/MgO NPs compared to $\text{TiC}_x/\text{Mg}/\text{MgO}$ NPs, where the thermodynamics and growth rates of the Mg crystal planes dominate the final shape. Finally, it is demonstrated that the core shape of TiC_x and TiH_x is affected by the Mg/Ti target ratio (affecting the composition in the plasma), and the type of the trace gas employed. In the case of CH_4 the TiC_x core forms a triangular platelet, while in the case of H_2 the TiH_x core transforms into a hexagonal platelet. We elucidate the reason for the $\text{TiC}_x/\text{TiH}_x$ core shape based on the presence of (i) defects, and (ii) hydrogen and carbon adsorption on {111} planes that alter the growth rates and surface facet stabilization.

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Introduction

Magnesium with its lightweight and high gravimetric capacity of 7.7 wt% for hydrogen has attracted strong interest for potential use as a hydrogen storage material.¹ Though it is a promising material, it suffers from poor kinetics and thermodynamics of hydrogen absorption/desorption. Kinetics has

been improved by nanostructuring, alloying and by adding catalysts.^{2–4} Interestingly, Mg based alloys consisting of immiscible elements *e.g.* Ti that was synthesized using a non-equilibrium synthesis method appeared to improve the kinetics for thin films, and ball-milled particles with good reversibility.^{5–7} It has been concluded that the cubic-based fluorite structure of MgTiH_x compared to tetragonal-rutile structure of MgH_2 is the important reason behind the improvement.^{5,8–10} The synthesis of immiscible bimetallic NPs using a non-equilibrium method based on gas phase synthesis is interesting because it opens a broad range of elements that can be tried, and also has a clear advantage in synthesizing different structural motifs over other synthesis methods.^{11–13} However, the thermodynamic stability of MgH_2 with its enthalpy of formation of -75 kJ mol^{-1} is a formidable barrier for applications and still remains an important challenge to overcome.¹ It is believed that the reduction in enthalpy of MgH_2 can effectively

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†Electronic supplementary information (ESI) available: Experimental details including target arrangement, gas phase synthesis set up, and effects of oxidation on MgTi NPs produced using H_2/CH_4 and EDX information. See DOI: 10.1039/c7nr06771b

reduce the temperature of desorption to a much lower value that is interesting for practical use. Although with spark plasma synthesis of MgTi nanocomposites the enthalpy of MgH_2 was reduced to -45 kJ mol^{-1} , despite the better hydrogenation kinetics it did not show the corresponding reduction in desorption temperature.¹² On the other hand, gas phase synthesis of MgTi NPs using an evaporation method did not show any reduction in the enthalpy of MgH_2 , though they showed improved kinetics of hydrogenation and dehydrogenation.¹³ Similarly, other reports on Mg NP confinement in a matrix/scaffold, which showed the reduction in enthalpy, considered that the effect of enthalpy reduction is compensated or counterbalanced by the entropy reduction, which finally does not affect the desorption temperature to the expected value.^{14–16} The reason for these differences is still not well understood. Hence, in order to understand the underlying reason for such differences, a good control over the synthesis method is necessary for tuning size, shape, composition and interface of each individual NP to unravel the corresponding effect on enthalpy. Although such studies on the effect of size and shape of Pd NPs have been performed earlier that showed the change in hydrogen absorption behavior compared to the one of bulk Pd,^{17–19} extending these methodologies to Mg based NPs is still very challenging. Moreover, the effect of shape, size and various structural motifs of MgTi ensemble NPs on hydrogen storage properties are also still missing, as there is lack of knowledge on controlling the nucleation of MgTi nanoparticle synthesis. Understandably, a detailed analysis of the interface, shape, structure, strain and orientation is a key to unravel the nanoscale effect on MgH_2 destabilization on a single MgTi NP.

In this respect, the gas phase synthesis based on DC magnetron sputtering in comparison to other gas phase methods has attracted attention for the controlled production of NPs with tailored size, composition and various structural motifs for both bi- and tri-metallic NPs.^{20–22} Nevertheless, extending to Mg based nanoparticles is still challenging due to the difficulty of Mg nucleation and its high affinity for oxygen.^{21–23} Moreover, controlling one specific structural motif over other structural motifs in combination with a uniform deposition of NPs on a substrate also remains a challenge. Nevertheless, we recently reported that the nucleation issue of bimetallic NPs and especially Mg can be solved, and their corresponding NP production rate can be enhanced and maintained for several hours of deposition by addition of trace gas.²³ Specifically, the addition of H_2/CH_4 as a trace gas for nucleation, along with tuning structural motifs, is interesting because it could favor the *in situ* formation of hydride NPs in the plasma depending on the element used.

In this work we studied extensively the influence of H_2 and CH_4 on the nucleation and growth of MgTi NPs, with the main focus on controlled synthesis and structural analysis of NPs using TEM. This type of in-depth structural analysis of MgTi NPs by means of TEM has not been reported yet, and it is essential for the ongoing research for hydrogen storage systems. For instance, we show that by altering the Ti concen-

tration the NPs structural motif is either alloyed MgTi or $(\text{TiC}_x/\text{TiH}_x)\text{-Mg}$ core-shell, for which the dimensions can be further tuned by changing the Ti concentration or the residence time in the aggregation chamber where the NPs are grown. This study demonstrates that the nucleation and growth of MgTi NPs can be controlled and tuned to have a multitude of structural characteristics, such as crystal structure, structural motif, size and shape that are useful for various applications *e.g.* solid state hydrogen storage, catalysis, plasmonics, switchable mirrors *etc.* Finally it will be shown that the produced NPs show a uniform distribution for their size and their structural motifs throughout the sample.

Results and discussion

Fig. 1(a) shows a Bright Field TEM image of MgTi NPs synthesized using a section target of Mg and Ti. The size of the produced NPs is approximately 40 nm, and shows a hexagonal shape in projection of the hexagonal closed packed (HCP) crystal structure. The HCP structure was confirmed by resolving the low index $\{10\bar{1}0\}$, $\{0002\}$ and $\{10\bar{1}1\}$ planes from the SAED pattern shown in Fig. 1(b). The NPs have a composition of $88 \pm 3 \text{ at\% Mg}$ and $12 \pm 3 \text{ at\% Ti}$ as measured by EDX. The projection of the NP along the Mg $[0001]$ axis shown in Fig. 1(c), indicates that the NP is faceted by the $\{10\bar{1}i\}$ planes, where i is an integer, *i.e.* the prismatic or pyramidal planes. Furthermore, the particles are often viewed along the Mg $[0001]$ direction, which suggests that the NPs are also termi-

Fig. 1 (a) Bright-Field TEM image of $\text{Mg}_{88}\text{Ti}_{12}$ NPs grown in an Ar gas environment, and (b) their corresponding SAED pattern. (c) Bright-Field high magnification TEM image of an $\text{Mg}_{88}\text{Ti}_{12}$ NP, and (d) its corresponding SAED pattern viewed along the $[0001]$ axis of Mg. The HCP MgTi and FCC MgO planes are indexed in white and yellow, respectively.

nated by $\{0002\}$ facets. The single NP SAED pattern shown in Fig. 1(d) shows also the presence of an MgO shell with $\{220\}$ planes that confirms the presence of crystalline oxide shell. The presence of a thin crystalline MgO shell of MgTi NPs is similar to pure Mg NPs as reported earlier,^{24–26} being important for their relatively high stability.

A series of bright field TEM images captured over a large tilt angle range (-65 to $+65$ degrees) are 3D reconstructed (tomography) to obtain a 3D visualization of the NP shape, as shown in Fig. 2. The NP shape resembles very well a truncated hexagonal pyramid where the facets consists mainly of $\{10\bar{1}1\}$ and $\{0002\}$ planes. Indeed, HRTEM viewing along a direction orthogonal to the $[0001]$ direction (Fig. S1 ESI†) shows that the (0002) plane is parallel to a facet. Notably, viewing along this direction confirms that the side facets are not parallel to the Mg $\{10\bar{1}0\}$ planes as it was observed for pure Mg NPs,²⁵ but rather are Mg $\{10\bar{1}1\}$ planes. The MgTi NPs were only synthesized using Ar as a sputtering gas without the supply of any trace gas. It must be stressed that the NPs shown in Fig. 1 were observed only a few times during NP deposition as most of the NPs produced have a core/shell (Ti/Mg) structural motif. The observed structural motif in the latter case was due to a formidable limitation of Mg nucleation that we recently reported.²³

The thermodynamic equilibrium shape of pure Mg and Ti crystals has been predicted by applying the Wulff construction based on DFT calculations of surface energies. The fractional contribution of the predicted surface planes for Mg have been estimated to be 38% $\{10\bar{1}1\}$, 37.8% $\{10\bar{1}0\}$ and 24.2% $\{0001\}$, whereas Ti consists of 55.5% $\{11\bar{2}1\}$, 24.5% $\{10\bar{1}1\}$, 17.2% $\{0001\}$, and 2.8% $\{10\bar{1}0\}$ planes.²⁷ Note that Mg is predicted to be faceted as a hexagonal prism, while Ti is predicted to form

a hexagonal pyramid and in both cases truncating the vertices reduces the surface energy. The former prediction corresponds well with previous observations of Mg NPs, while the combination of the two is similar to what is observed for MgTi NPs as it is shown in Fig. 2(c). This implies that a slight amount of Ti present in the particle as a solid solution affects the surface energy of particular crystal planes. Therefore, the alloyed structure increases the $\{10\bar{1}0\}$ surface energy, while decreasing the $\{10\bar{1}1\}$ surface energy. This results in an NP shape that is predominantly terminated by the $\{10\bar{1}1\}$ and $\{0002\}$ facets.

Fig. 3 shows the effect of methane as a trace gas to initiate and sustain the MgTi nucleation process, which otherwise ceases as Mg and Ti stop nucleating.²³ Fig. 3(a and b) shows a Bright-Field TEM image of MgTi NPs synthesized using CH_4 with a section target of $\frac{3}{4}\text{Mg} + \frac{1}{4}\text{Ti}$. The corresponding SAED pattern in Fig. 3(c) shows that the MgTi NPs are a solid solution of Mg and Ti. This can be confirmed by the interplanar “ d ” spacing measured from the diffraction pattern, which shows a clear deviation from pure Mg similar to our previous work.²³ Once the target composition is changed to increase the Ti concentration ($\frac{1}{2}\text{Mg} + \frac{1}{2}\text{Ti}$), the MgTi NPs produced shows a core/shell structural motif. The target composition was changed due to the very low concentration of Ti observed in the NPs produced in the case of $\frac{3}{4}\text{Mg} + \frac{1}{4}\text{Ti}$. Moreover, the increase in Ti concentration also modifies the MgTi NP final structure from HCP to FCC, where for the latter the formed hydride has better absorption kinetics than the former.^{7,9} Fig. 3(d and e) and the diffraction pattern shown in Fig. 3(f) reveal that the core is made of TiC_x and the shell of Mg/MgO. HCP Mg is identified from the resolved low index $\{10\bar{1}0\}$, $\{0002\}$ and $\{10\bar{1}1\}$ planes with the corresponding interplanar distances that matches those of pure Mg. Although the SAED pattern is confirming HCP Mg as an intermediate shell, the presence of trace amounts of Ti in the shell cannot be completely neglected. TiC_x is identified from a lattice with a face-centered cubic (FCC) symmetry as the $\{200\}$ and $\{220\}$ planes are visible. The lattice parameter of the FCC crystal structure is $4.40 \pm 0.04 \text{ \AA}$, which matches with the crystal structure of TiC ($a = 4.33 \text{ \AA}$). This analysis is indicating to the same scenario observed for MgNi and MgCu NPs produced without any trace gas as reported earlier. These studies showed that Mg rich region grows on Ni and Cu which act as core for MgNi and MgCu NP synthesis. Moreover, a detailed inspection of the core-shell NPs reveals an orientation relationship (OR) between the core and the shell. This is deduced from a single NP SAED pattern (Fig. S2 ESI†). Viewing along the $[0001]$ axis of Mg, the $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ planes are visible. The TiC_x $\{220\}$ planes are also visible, and they are parallel to the Mg $\{11\bar{2}0\}$ planes when TiC_x is viewed along the $[111]$ axis. In projection, the Mg $\{10\bar{1}0\}$ planes are parallel to the NP facets, and the TiC_x $\{220\}$ planes are parallel to the core/shell interface as viewed along this axis. Therefore, the OR between the TiC_x core and Mg shell is given by $\text{Mg } [11\bar{2}0] // \text{TiC}_x [220]$ and $\text{Mg } \{0002\} // \text{TiC}_x \{111\}$ i.e. the HCP and FCC close-packed planes and the close-packed directions are parallel. Furthermore, identical to Mg NPs and alloyed MgTi NPs, the core/shell NP is

Fig. 2 3D reconstruction of the particle shown in Fig. 1(c). (a) Viewed along the $[0001]$ direction and (b) viewed along the $[10\bar{1}0]$ direction. (c) The NP's shape based on the 3D reconstruction and the SAED patterns of the present work.

Fig. 3 Bright-Field TEM image and SAED pattern of MgTi NPs synthesized using CH_4 as a trace gas and various section target ratios. (a, b) $\text{Mg}_{86}\text{Ti}_{14}$ NPs with solid solution structural motif produced using $\frac{3}{4}\text{Mg} + \frac{1}{4}\text{Ti}$. (d, e) $\text{Mg}_{85}\text{Ti}_{15}$ NPs with core/shell/shell structural motifs produced using $\frac{1}{2}\text{Mg} + \frac{1}{2}\text{Ti}$. (g, h) $\text{Mg}_{45}\text{Ti}_{55}$ NPs with core/shell structural motif produced using $\frac{1}{4}\text{Mg} + \frac{3}{4}\text{Ti}$. (c) Corresponding SAED pattern of (a, b) MgTi planes are indexed in black. (f) Corresponding SAED pattern of (d, e). (i) Corresponding SAED pattern of (g, h). The HCP Mg and FCC TiC planes are indexed in black and red, respectively.

enclosed by a thin MgO shell, where the OR is given by $\text{Mg} [0001]//\text{MgO}[001]$ and $\text{Mg} \{10\bar{1}0\}//\text{MgO} \{220\}$. The shape of the NPs appears to be identical to the alloyed NPs shown in Fig. 1, as SAED patterns of NPs in various orientations (Fig. S3 ESI†) yield the same result of particles being faceted by $\{10\bar{1}1\}$ and $\{0002\}$ planes.

As the Ti concentration is increased further with a $\frac{1}{4}\text{Mg} + \frac{3}{4}\text{Ti}$ section target, the MgTi NPs again transform into a core/shell structure with a clear TiC_x core and an MgO shell as it is shown in Fig. 3(g–i). Unlike the particles shown in Fig. 3(d and e), where the NPs have an intermediate Mg/Mg rich shell and a crystalline oxide, the present particles only show an amorphous MgO shell, as there are no crystalline MgO reflections in the SAED pattern and STEM-HAADF/EDX shows that the amorphous material that surrounds these NPs is MgO. Moreover, the shape of the NPs transforms to a platelet-like structure. Therefore, this is a clear confirmation of the effect of Ti/Mg vapour concentration on the TiC_x growth, and the formation of different structural motifs.

The faceting of the TiC_x core is affected by changing the Mg/Ti ratio as it is noted by the change of shape. For Mg-rich NPs the surfaces are mainly $\{10\bar{1}1\}$ and $\{0002\}$ planes of Mg, while the particle is faceted by the $\{111\}$ or $\{100\}$ planes of TiC_x when the concentration of Mg is low. These results point

to the growth of Mg on the TiC_x core that subsequently oxidizes to form an outer MgO shell. At high Mg concentration a significant amount of HCP Mg remains, whereas virtually all HCP Mg is consumed by the oxide formation at lower Mg concentrations. Furthermore, the growth of Mg on TiC_x is supported by the observation that the TiC_x core diameter remains approximately 20–25 nm, whereas the Mg shell reduces in size when the composition of the NPs becomes richer in Ti.

Fig. 4 shows MgTi NPs produced using H_2 as a trace gas to further investigate the effect of the gas environment on the nucleation, structure and shape of the produced NPs. Addition of H_2 as a trace gas will not only resolve the issue of nucleation but also can favour *in situ* formation of a hydride phase that is more desirable for hydrogen storage materials than the ones with a TiC_x core that is formed using CH_4 as a trace gas. Our experimental investigation with H_2 as a trace gas and a $\frac{1}{2}\text{Mg} + \frac{1}{2}\text{Ti}$ section target shows NPs in Fig. 4(a and b) with a solid solution structure. However, as the composition of the target is increased to 75% Ti (using a $\frac{1}{4}\text{Mg} + \frac{3}{4}\text{Ti}$ section target), the NPs produced have a core/shell structure of TiH_x/MgO as shown in Fig. 4(d and e). This structural motif resembles the NPs produced using CH_4 as a trace gas, which shows the formation of a TiC_x/MgO core/shell structure. Note that the addition of H_2 as a trace gas to a section target of $\frac{3}{4}\text{Mg} + \frac{1}{4}\text{Ti}$ also showed the

Fig. 4 Bright-field TEM image and SAED pattern of MgTi NPs synthesized using H_2 as a trace gas and various section target ratios. (a, b) $\text{Mg}_{86}\text{Ti}_{14}$ NPs with solid solution structural motif produced using $\frac{1}{2}\text{Mg} + \frac{1}{2}\text{Ti}$. (c) Corresponding SAED pattern showing the presence of HCP MgTi. (d, e) $\text{Mg}_{47}\text{Ti}_{53}$ NPs with core/shell structural motifs produced using $\frac{1}{4}\text{Mg} + \frac{3}{4}\text{Ti}$. (f) Corresponding SAED pattern of TiH.

solid solution structure similar to NPs observed with a section target $\frac{1}{2}\text{Mg} + \frac{1}{2}\text{Ti}$.

NPs with a higher Ti content as shown in Fig. 4(d and e) have a composition of 47 at% Mg and a mean diameter of 24 ± 5 nm. No clear shell of Mg or a Mg rich alloy is observed besides the 3–4 nm thick MgO shell. At high magnification void development beneath the MgO shell is observed which in some occasions led to a porous subshell (Fig. S4 ESI†), which can be explained by the oxidation associated Kirkendall effect.²⁵ Moreover, Mg-rich (around 70 at% Mg) NPs show the porous subshell (Fig. S4 ESI†) which shrinks in size for the Ti-rich (around 50 at% Mg) particles as shown in Fig. 4(c). Although voids and porous subshells were also found in the case of CH_4 , the effect of void formation is observed to be more prominent in the case of hydrogen. The SAED pattern in Fig. 4(f) reveals $\{111\}$, $\{200\}$ and $\{220\}$ planes so that the crystal structure is determined to be FCC with a lattice parameter of 4.45 ± 0.05 Å, which corresponds to the fluorite TiH_x crystal structure. Note that apart from STEM-EDX mapping we were able to distinguish between TiH_x and TiC_x , as the former was unstable under the electron beam in the TEM. Yet again, the low index HCP Mg planes are not visible in the SAED pattern. The shape of the NPs tend to be platelet like since the projections either form a disk or a rectangle, which is very similar to the NPs described before. However, the exact faceting cannot be determined, as the particles do not have sharp facets. SAED analysis can clearly distinguish between the presences of $\text{TiC}_x/\text{TiH}_x$ core of the NPs synthesized using CH_4 and H_2 as a trace gas. However, due to similarities in crystal structure and lattice parameters of many Ti compounds (e.g. TiO , TiC and TiN), and the error in SAED analysis, misinterpreta-

tions are likely to occur. Hence, the SAED patterns are complemented with STEM-EDX maps and STEM-EDX line profiles as shown in Fig. 5, which allow with greater certainty to determine and confirm the type of Ti compound present in the core.

Fig. 5(a) and (b) show a STEM-HAADF image, an EDX mapping of a $\text{TiC}/\text{Mg}/\text{MgO}$ core/shell/shell NP and the extracted EDX line profile, which confirm the presence of TiC_x as a core followed by an Mg rich intermediate shell, and an MgO shell. Moreover STEM-EDX mappings were carried out on different NPs that were freshly synthesized with identical parameters. The NPs are showing core/shell structural motifs, where besides the normal hexagonal cores observed in Fig. 3(d and e) a few triangular cores (in projection) were also observed. Nonetheless, the core/shell structural motifs are supported by the STEM-HAADF images, and the STEM-EDX maps reveal that the core is indeed TiC_x surrounded by an Mg rich shell. Fig. 5(c) and (d) show a STEM EDX map and an EDX line profile of TiH_x/MgO NPs confirming the presence of a Ti rich core and MgO as a shell. Although H cannot be mapped using STEM-EDX, a comparatively lower concentration of C in the NPs indeed suggests the formation of TiH_x as a core rather than TiC_x . Moreover, comparison of quantified STEM-EDX spectra of cores in the NPs produced with CH_4 and H_2 reveals that the percentage of C is around 40–50 at% and around 5–20 at%, for CH_4 and H_2 based NPs, respectively. This further corroborates that the cores for the H_2 based NPs likely consist of TiH_x .

Comparing the influence of CH_4 and H_2 as trace gases, it is evident that the formation of TiC_x is more profound even with lower concentration of Ti than that observed with H_2 to form

Fig. 5 (a) STEM-EDX mapping of $\text{TiC}_x/\text{Mg}/\text{MgO}$ NP. (b) Corresponding EDX-line profile of the NP, averaged over the width of the box indicated in the HAADF image. (c) STEM-EDX mapping of TiH_x/MgO NP. (d) Corresponding EDX-line profile of the NP.

TiH_x . This can be a direct consequence of the interaction of C and H atoms with Ti atoms during the synthesis condition of NPs. Moreover, addition of CH_4 during synthesis in a plasma environment is a conventional method to produce TiC_x thin films and NPs.^{28–30} However, for our purposes, we use only a trace level of these gases to see the effect on the nucleation once the homogenous nucleation completely stops. The nucleation and growth of these NPs can be explained by either homogeneous or heterogeneous nucleation, or a combination of both. In this particular case CH_4 decomposes in the plasma to C and H so that the supersaturated Ti vapour nucleates in an Ar- CH_4 gas to form TiC_x clusters. Despite decomposing in four H atoms and only one C atom, TiC_x is formed more likely due to the lower (more negative) Gibbs free energy of TiC (-180 kJ mol^{-1})³¹ as compared to TiH_2 (-113 kJ mol^{-1}).³²

Alternatively, TiC_x nucleation could also be explained due to target poisoning and heterogeneous nucleation.³⁰ At sufficient partial pressure of CH_4 , C adsorbs on the Ti target and forms a thin TiC_x surface layer. For example, the monolayer formation time at the trace level of CH_4 and H_2 is very roughly of the order of seconds. This effect is supported by the fact that the sputtering voltage increases several tenths of volts the moment when the target is subjected to a CH_4 gas flow. An increased sputter voltage indicates that more energetic Ar ions have to compensate for the increased binding energy of

surface atoms *i.e.* TiC_x has a lower sputter yield compared to Ti due to the covalent/ionic character of TiC_x . Moreover, nucleation continues for several seconds when inflow of methane is stopped, and evacuated from the system, indicating the erosion of the contaminated surface layer. During cooling and transport by the Ar gas flow Mg condenses on the TiC_x seeds to form a core/shell particle, since high melting point materials tend to nucleate first.¹¹ Moreover, the dimer binding energy of diatomic Ti-C is 4.384 eV and that of Ti-H, 2.1141 eV, which shows that the formation of TiC nuclei is favoured in comparison to TiH.²³

In addition to enthalpy of formation and binding energy, TiC formation is generally favoured at high temperature in comparison to TiH_2 , which forms only during cooling and low temperature.³³ This can also be one of the reasons that can lead to the formation of TiC, though there are four H atoms available for TiH formation. Moreover, we also observe that the formation of solid solution structures is relatively easy to achieve only when the Ti composition of the target is less for *e.g.* $\frac{3}{4}\text{Mg} + \frac{1}{4}\text{Ti}$ target, and irrespective of the trace gas employed. But as the Ti concentration is increased, the formed NPs and their structural motifs are changed depending on the interaction with trace gas. Fig. 6 shows a schematic of the effect of the section target ratio on the MgTi NP production and their structural motifs. In our recent article,²³ we indi-

Fig. 6 Schematic of the nanoparticle deposition system and the effect of trace gas and Ti section target ratio on the evolution of MgTi structural motifs.

cated that H₂ favours the formation of a solid solution compared to CH₄ for a section target of ($\frac{1}{2}\text{Mg} + \frac{1}{2}\text{Ti}$) ratio. However, from the present study we learned that the formation of such structures depends on the concentration of Ti and Mg in the plasma and their particular interaction with the trace gas. This is a complex process and its comprehensive understanding is still missing.

Our results show that many structural characteristics of MgTi NPs depend strongly on the composition of the target and the choice of trace gas. In most cases the MgTi NPs form a core/shell structure, where an Mg and MgO shell surround a TiC_x or TiH_x core, and in some cases a solid solution of MgTi is observed. To understand further how these NPs obtain their motifs, it becomes important to relate the target composition and the type of trace gas employed to the nucleation and growth process. For the core/shell NPs it is necessary to know if this core/shell structural motif originates from a sequential growth mechanism or from phase separation. In recent works we have demonstrated that a solid solution of immiscible MoCu NPs does not phase separate when the plasma temperature is low due to a low sputtering current of 0.250 A.¹¹ When also considering the nucleation issue of Mg and Ti, a sequential growth process looks more favorable than phase separation. Furthermore, simulations have already demonstrated that spherical symmetry, as observed in this study, can hardly be the result of phase separation.³⁴ Also the orientation relation between the TiC_x core and Mg shell (for the $\frac{1}{2}\text{Mg} + \frac{1}{2}\text{Ti}$ target) is an indication that the core/shell structure is a result of epitaxial growth rather than phase separation. In addition, in order to provide more support for this claim we opt for a generic geometrical model where we compare the expected core/shell dimensions as a function of composition with the experimentally determined dimensions of the core/shell NPs. The assumption of this model is that complete phase separ-

ation is most likely impossible on the timescale of the residence time of the NP in the aggregation chamber, as the diffusion rate is low due to the low thermal energy provided by the low sputtering current of 0.250 A as mentioned in earlier studies.¹¹

Indeed, the geometrically predicted NP core/shell dimensions as a function of MgTi composition compare reasonably well with the experimental results (core diameter approximately 25 nm) as shown in Fig. 7. Note that the two data points, which are very close to the minimum size of the NP (which is constrained by the MgO thickness and core diameter), are exactly those which have no clear Mg shell in bright field TEM images. Therefore, the main growth mechanism is considered to consist of two spatially and temporally separated nucleation and growth processes. According to this process, tuning the relative concentration of Mg and Ti and their residence time in the aggregation chamber can control the dimension of the core/shell NPs. The former control is achieved by changing the composition of the sectioned MgTi target from $\frac{1}{2}\text{Mg} + \frac{1}{2}\text{Ti}$ to $\frac{1}{4}\text{Mg} + \frac{3}{4}\text{Ti}$ that results in a thinner Mg shell. The latter is achieved by reducing the length of the aggregation chamber where the NPs grow, so that their growth time is limited. In this case, as expected, the NPs do not have an Mg shell, but only an MgO shell after oxidation. Note that in the case of the $\frac{1}{4}\text{Mg} + \frac{3}{4}\text{Ti}$ target the Mg vapor density is lower compared to the $\frac{1}{2}\text{Mg} + \frac{1}{2}\text{Ti}$ target. As a result no Mg shell is observed, and as the aggregation length is reduced the concentration of Mg is further reduced in the NP. Another effect of reducing the Mg shell thickness is that the shape of the core dominates the overall NP shape. When the Mg shell is sufficiently thick (in the case of $\frac{1}{2}\text{Mg} + \frac{1}{2}\text{Ti}$ target and CH₄ trace gas) the NP shape is determined by thermodynamics and the growth rates of the Mg crystal planes. However, as the Mg shell becomes thinner (in the case of $\frac{1}{4}\text{Mg} + \frac{3}{4}\text{Ti}$ target) Mg grows parallel to the core's facets and follows the same shape of the core.

Finally, these results indicate that the TiC_x/TiH_x core forms independently of the Mg shell, and neither Ti concentration nor the length of the aggregation chamber affects its size significantly. This is a direct proof that the core is formed closer

Fig. 7 Geometrically predicted size-composition relation of sequential growth mechanism compared with the experimental observations.

to the sputtering target, and that condensation of Mg on the core occurs farther away from the target as it is evident from the variation in aggregation length. Interestingly, the core diameter remains approximately the same despite the higher Ti concentration (larger target fraction Ti) and shorter growth time (smaller aggregation length). Especially the former suggests that the core growth rate is either restricted by the CH_4 or H_2 supply, or the Mg vapor condenses at a certain distance from the target independent of its density in the gas phase, for instance due to the similar temperature gradient in the plasma. Overall, we believe that there is sufficiently strong experimental and computational evidence that supports the sequential growth mechanism where a $\text{TiC}_x/\text{TiH}_x$ core is formed first, followed by condensation of an Mg shell during subsequent growth of the NPs.

The sequential growth mechanism is predominantly related to the issue of Mg and Ti nucleation and binding energy of Mg–Mg and Ti–C/Ti–H as we have indicated earlier.²³ In addition, comparison of NPs produced by varying the composition of Ti (50 and 75% target percentage) results in various different structural motifs, *e.g.* core/shell, core/shell/shell, and solid solution depending on the trace gas employed, as is shown in Fig. 3 and 4. In the particular case of CH_4 we observe that the increase in target composition of Ti from 50% to 75% leads to structure changing from $\text{TiC}/\text{Mg}/\text{MgO}$ to TiC/MgO , respectively. This also compares well for H_2 as a trace gas in the case of a target composition of 75% for Ti. Therefore in both cases the formation and nucleation of NPs are rather similar, and we can arguably mention that the reduction of the Mg composition in the section target is the main reason for this structural variation. This can be understood as a consequence of the reduced density of Mg atoms in the plasma due to the $\frac{1}{4}\text{Mg}$ composition ratio of the target. Furthermore, during the growth process, the Mg vapor condenses on TiC_x and is distributed among various TiC_x NPs leading to TiC/MgO after complete oxidation of the Mg shell.

Because the final shape of the NPs depends on the shape of the $\text{TiC}_x/\text{TiH}_x$ core, it is important to understand why there is a slight difference in core shape for the different deposition settings. Although the diameter of the TiC_x core remains approximately equivalent and independent of the Ti concentration and the aggregation chamber length, the exact shape and faceting change. Although it has a projected hexagonal shape along the $[111]$ axis and an aspect ratio of ~ 1 for the target $\frac{1}{2}\text{Mg} + \frac{1}{2}\text{Ti}$ as is shown in Fig. 3, it is hexagonal or triangular shape along the $[111]$ axis (for H_2 and CH_4 , respectively) when the target is $\frac{1}{4}\text{Mg} + \frac{3}{4}\text{Ti}$ as shown in Fig. 8. Especially, when hydrogen is used as a trace gas in the case of a $\frac{1}{4}\text{Mg} + \frac{3}{4}\text{Ti}$ target, the NPs obtain a platelet-like shape (aspect ratio of ~ 0.5) as shown in Fig. 8(c) & (d). This is not a thermodynamically preferable shape to reduce its surface energy as the surface area is large for these structures. Similarly, when the trace gas is CH_4 , the particles also have an aspect ratio below unity, but larger than of 0.5 as shown in Fig. 8(a). Both of the resulted shapes cannot be formed unless planar defects such as stacking faults or multiple twin planes are playing a

Fig. 8 (a) High magnification Bright-Field TEM image of a $\text{Mg}_{66}\text{Ti}_{34}$ NPs of size 44 ± 6 nm produced using CH_4 and $\frac{1}{4}\text{Mg} + \frac{3}{4}\text{Ti}$ and deposited with a triangular shape in projection (b) corresponding single NP SAED pattern viewed along the TiC_x $[111]$ axis. Note that the very faint spots at $1/3\langle 422 \rangle$ are shown in square box. (c) & (d) High magnification Bright-Field TEM images of $\text{Mg}_{64}\text{Ti}_{36}$ NPs of size 28 ± 7 nm produced using H_2 and $\frac{1}{4}\text{Mg} + \frac{3}{4}\text{Ti}$. (c) Rectangular shape in projection, and (d) the corresponding SAED pattern viewed along the $[11\bar{2}]$ axis. (e) Hexagonal shape in projection, and (f) the corresponding SAED pattern viewed along the $[111]$ axis.

role in the formation of the platelet seed.^{35,36} Moreover, combining the NP shapes with the single NP SAED pattern where the features of stacking faults of $\{111\}$ planes are observed, leads to the conclusion that stacking faults of $\{111\}$ planes for higher Ti concentration are the reason for the platelet shape of the $\text{TiC}_x/\text{TiH}_x$ core. Stacking faults are more commonly observed in the case of FCC metals as they have the lowest energy for stacking fault formation,³⁶ but in the case of TiC the stacking fault energy is high.³⁶ Therefore, unless the stacking fault energy is reduced, its formation is rather improbable.

Earlier articles have reported that carbon vacancies in TiC can reduce the stacking fault energy.³⁷ In addition, there are reports stating the presence of impurity *e.g.* Al, B is playing a role in the platelet morphology formation of TiC.³⁸ However, the impurity level in TiC does not match in our case for a

similar observation. Apparently from our observation the formation of stacking faults is only possible when the Ti concentration is high, and even more pronounced when H_2 is used as compared to CH_4 . As the nucleation rate during the synthesis of the NPs (from $\frac{1}{4}Mg + \frac{3}{4}Ti$ target) remains of the same order of magnitude as compared to the NPs that do not have stacking faults (from $\frac{1}{2}Mg + \frac{1}{2}Ti$ target), the number density of nuclei is also of the same order of magnitude. Hence, despite the higher density of Ti atoms in the plasma, no significant increase in nucleation rate occurs. This is also consistent with the observation that virtually no change in TiC_x/TiH_x core diameter occurs when the Ti concentration is increased, suggesting a nucleation rate limited growth process. Therefore, due to a limited supply of C the excess of Ti in the vapor can condense on the $\{111\}$ planes of the TiC_x/TiH_x nuclei inducing defects such as stacking faults when the target is $\frac{1}{4}Mg + \frac{3}{4}Ti$. Furthermore, from literature it is also known that hydrogen can induce defects during growth, which is consistent with the lower aspect ratio of these NPs.

The triangular shape in projection along the $[111]$ axis of NPs produced with CH_4 suggests that the TiC_x core is faceted by $\{111\}$ planes as the six-fold presence of $\{220\}$ type reflections is visible in the SAED pattern shown in Fig. 8(b). The sides of the NP is faceted by $\{111\}$ or $\{100\}$ planes, that yield a three dimensional tetrahedral shape. Moreover, from Fig. 8(a) and the corresponding diffraction pattern in Fig. 8(b), it contains $1/3\{422\}$ reflections marked in squares, which are usually forbidden for an FCC lattice. These forbidden reflections are also observed in the case of Pd, Ag and Au nanostructures grown in the form of thin plates confirming the presence of platelet-like morphology.^{36,39–41} For gas phase grown TiC_x NPs it has been shown that their shape is not controlled by their stoichiometry, but by the growth rates of the $\{111\}$ and $\{100\}$ planes, which are directly affected by C adsorption.²⁹ Moreover, the authors elucidated that the growth rate of the $\{111\}$ planes can be completely inhibited or varied by the carbon concentration and by their adsorption, yielding NPs with a combination of $\{100\}$ and $\{111\}$ facets or terminated only by $\{111\}$ facets.²⁹ Hence, in our case the $\{111\}$ faceted TiC_x core is more likely caused by kinetically restricted growth of $\{111\}$ planes due to carbon adsorption.

On the other hand, the truncated triangular or hexagonal-like shape in projection along the $[111]$ axis of NPs produced with H_2 , indicates that in this case there are $\{111\}$ and $\{100\}$ facets. Note that again this is not a thermodynamically favored shape, as DFT calculations have shown that the fluorite TiH_2 has the lowest surface energy when faceted by $\{111\}$ planes, and the surface energy of the $\{100\}$ planes is nearly twice that of the $\{111\}$ planes.²⁷ Hence, in this case perhaps a similar effect occurs where the growth rate of the $\{111\}$ planes is restricted. Similar observations are also noticed in the case of Ni, where the H_2 adsorbed on the surface alters the surface energy of closed packed planes.⁴² It was observed that the surface with lowest surface energy for Ni had changed from $\{111\}$ to $\{100\}$. And also during an intermediate transition the surfaces were composed of both $\{111\}$ and $\{100\}$ surfaces,

respectively. Moreover, in the wet chemical synthesis of NPs, by products released during the chemical reaction play a significant role in the final morphology of the crystal, and it was reported that H_2 plays a role in the synthesis of cubic Pt NPs, where H_2 adsorption stabilizes the $\{100\}$ facets.^{43,44} Therefore, in our case the H_2 also plays a significant role in obtaining the hexagonal platelet structure. Alternatively, for various FCC NPs it has been argued that stacking faults of the basal plane cause an asymmetry of the geometry of the six side facets of the NP, yielding asymmetrical growth rates.^{36,39} The seed is believed to form a hexagonal platelet with a stacking fault in the basal plane, and having alternating $\{100\}$ and $\{111\}$ side facets. These side facets have an inward or outward geometry, which affect the growth rates. Hence, when this asymmetry persists (for instance by one twin plane) half of the side facets grow faster and result in a triangular shaped NPs. If, however, multiple stacking faults are present, the asymmetry in growth rates of adjacent side facets is lost, and hexagonal NPs are formed again.

Conclusions

In summary, we have shown the effect of CH_4 and H_2 as a trace gas on the MgTi nucleation and growth sequence, which allows tuning of the structural motifs and shapes of MgTi NPs. We particularly show the effect of Ti concentration and trace gas interaction on the synthesis of various structural motifs by increasing the section target composition of Ti from 25%, to 75%. In depth SAED pattern analysis of the produced MgTi NPs, and tomography measurements based on a tilt series of TEM Bright-Field images show that the shape of the MgTi alloy NPs is a truncated hexagonal pyramid. Moreover, we prove the formation of various MgTi structural motifs based on the sequential growth mechanism, which matches very well with our calculated generic geometric model. The proposed sequential growth mechanism of the above structural motifs was due to the inadequacy of Mg to nucleate in the synthesis condition. Furthermore, we show the crucial effect of the TiC_x core shape on the shape evolution of the final TiC_x/MgO and TiH_x/MgO NPs as compared to $TiC_x/Mg/MgO$ NPs. The shape of the latter is dominated by the thermodynamics and growth rates of the Mg crystal planes, which proves the effect of Mg concentration and the sequential growth mechanism on the shape evolution of NPs.

Experimental methods

Synthesis

The MgTi bimetallic nanoparticles with various structural motifs were produced by a home modified nanoparticle deposition system Nanogen 50 from Mantis Deposition Ltd (<http://www.mantisdeposition.com>). The sample chamber was evacuated to a base pressure of $\sim 1 \times 10^{-8}$ mbar with an oxygen partial pressure of ($\sim 10^{-11}$ mbar). Supersaturated metal vapor

is produced by magnetron sputtering of a sectioned target (99.95% purity of the Mg and Ti as obtained from Alpha Aesar) shown in Fig. S6 of the ESI† in an inert Argon atmosphere pressure of ~0.25 mbar with a 0.250 A discharge current. The supersaturated metal vapor is then cooled by Ar 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 that acts as a drift and sputter gas. For varying the structural motifs and shape of MgTi NPs, CH₄/H₂ trace gas was introduced by means of a high precision UHV-leak valve directly in the aggregation chamber up to a pressure of $\sim 6 \times 10^{-4}$ mbar. Direct measurement of the CH₄/H₂ partial pressure during sputtering was not feasible because the magnetron is operated at a high Ar pressure for sputtering (0.25 mbar).

TEM analysis

The nanoparticles transported from the aggregation volume were deposited onto 25 nm thick Si-nitride membranes or carbon coated Cu grid, which were used for Transmission Electron Microscopy (TEM) analysis in a JEOL 2010F TEM. Tomography measurements were done in FEI Technai T20 using a dedicated tomography holder. HAADF-STEM-EDS studies were performed using a probe-corrected JEOL ARM, operated at 200 kV, equipped with a 100 mm² Centurio EDS detector.

Conflicts of interest

There are no conflicts to declare.

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