



Article Hydrogen Assisted Magnesiothermic Reduction of Y-Doped, Nanocrystalline TiO₂

Hank Lloyd, Ying Xu * D and Peng Cao * D

Department of Chemical and Materials Engineering, The University of Auckland, Private Bag 92019, Auckland 1142, New Zealand; hllo538@aucklanduni.ac.nz

* Correspondence: sherry.xu@auckland.ac.nz (Y.X.); p.cao@auckland.ac.nz (P.C.)

Abstract: The direct reduction of TiO₂ to low-oxygen titanium metal is achievable via Hydrogen Assisted Magnesiothermic Reduction (HAMR). To investigate and leverage the oxygen-scavenging properties of rare-earth dopant species on the HAMR process, Y-doped and undoped TiO₂ powders were synthesized and characterized. HAMR blends incorporating the synthesized TiO₂ were reduced under forming gas atmospheres. X-ray powder diffraction (XRD) and scanning electron microscope (SEM) characterization was performed prior to and following reduction. The TiO₂ powders were observed to be dense and nanocrystalline. Following reduction, more extensive development of intermediate HAMR phases was observed as a result of Y-doping. The microstructure/phase evolution of the HAMR reduction phases was observed to deviate from the expected for dense TiO₂ particles. Rapid restructuring of the TiO₂ particle interiors was attributed to increased bulk diffusion rates of nanocrystalline materials. Doped nanocrystalline TiO₂ powders were identified as potential alternative feedstocks for HAMR experiments. The byproduct MgO phase was observed to grow as a particle agglomerating network that is dense when formed at 750 °C and porous when formed at 900 °C.

Keywords: HAMR; nanocrystalline TiO₂; Y-doped TiO₂; reduction; magnesium

1. Introduction

Titanium metal offers attractive strength to weight ratios and corrosion resistance, suiting aerospace and chemical plant applications [1]. However, extensive industrial use of titanium has been limited by the high energy cost of the Kroll production process. The Hydrogen Assisted Magnesiothermic Reduction (HAMR) of TiO_2 has attracted considerable research attention as an alternative, competitive method to produce low-oxygen titanium metal without the Kroll process's extensive vacuum and arc remelting stages. HAMR further presents a relatively low-temperature processing route [2–5].

Magnesium metals can thermochemically reduce TiO₂ to titanium metal with levels of dissolved oxygen of 2 wt % O at 750 °C. This reduction limit is determined by the thermodynamic stability of titanium-oxygen solid solutions [6]. Dissolved oxygen is highly detrimental to the ductility of titanium. ASTM grade 4 titanium—the highest oxygen content of unalloyed Ti—specifies a maximum of 0.4 wt % O [1]. Note that oxygen is considerably soluble in α -phase titanium, as may be observed in the corresponding phase diagram [7].

The principle underlying the Hydrogen Assisted Magnesiothermic Reduction (HAMR) of TiO_2 is the destabilization of Ti-O solid solutions via temporary alloying with hydrogen, extending the deoxygenation limit of TiO_2 with magnesium. Note that while calcium metal is able to reduce TiO_2 to lower levels of dissolved oxygen than magnesium (0.03 wt % O at 750 °C), the preferred reducing agent is magnesium, due to its lower cost [8]. Utilizing HAMR, titanium powders meeting ASTM grade B299 (0.15 wt % dissolved oxygen) have been synthesized [9].

The phase evolution of the HAMR process has been studied in detail with large, dense, highly crystalline TiO_2 particles [5,8]. The reduction occurs via a series of solid-state



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). transformations. Magneli phases (of formula Ti_XO_{2x-1}) and magnesium-titanite phases (primarily MgTiO₃) form first. The magnesium-titanites grow as needle-like phases that migrate into TiO₂ particle cores. Lefler et al. posit that the inter-needle space is comprised of the terminal phase of the Magneli series: Ti_2O_3 . Following this, both the magnesium-titanite and Ti_2O_3 phases are converted to TiO, a stage that requires local rebuilding of the particle lattice. This presents a fine, sponge-like 'rebuilt shell' that migrates to the particle core. The TiO phase is further reduced to the solid solutions Ti(O) or Ti(O)(H). Fresh Mg is required to progress each stage and is converted to byproduct MgO. An exception is seen in the uptake of MgO by Magneli phases to produce more oxygen-deficient Magneli phases and magnesium titanites [8]. Figure 1 demonstrates the phase transformations schematically.



Figure 1. Schematic of the HAMR Phase Transformation Process (Adapted from [8]).

The HAMR process is performed in three stages. The first stage—reduction—is used to reduce/remove the majority of the oxygen from the TiO₂ matrix, producing a mixture of Ti(O)(H), byproduct MgO, and MgCl₂ powders. The reduced powders are then leeched with dilute HCl to remove the MgO. Optionally at this stage, the Ti(O)(H) powders may be granulated and sintered to control the next stage's powder particle shape, size distribution, and porosity. The Ti(O)(H) powders are then blended with Mg and MgCl₂ and inputted to the deoxygenation stage, which removes the remaining dissolved oxygen to produce Ti(H) powders and more byproduct MgO. The deoxygenated powders are then leeched again before dehydrogenation. The dehydrogenation stage entails heating Ti(H) powder in a vacuum or inert atmosphere to reverse the temporary hydrogen alloying of the HAMR process [8,9].

Doped TiO₂ has seen extensive research in photocatalytic applications. The production and characterization of Y-doped TiO₂ from the hydrolysis of Titanium Tetrabutoxide has been well documented [10,11]. Titanium alloys with rare-earth elements have been investigated—specifically, rare-earth element alloying ingredients have been investigated as strong scavengers of oxygen and/or chlorine impurities. Y has been observed to form desirable, fine nanodispersoids of Y₂O₃ that strengthen Ti matrices [2].

In the present work, by the rational that Y provides a desirable, oxygen scavenging alloying ingredient to strengthen low-oxygen titanium, Y-doped TiO₂ was input as a feedstock to the HAMR process. The initial stage (the reduction stage) of HAMR was investigated to determine if Y-doping affected the reduction of TiO₂. Further, it was desired to see if Y dopant would produce phases advantageous to the further processing of reduced Ti powders. A 100% H₂ atmosphere was omitted, as it was desired to investigate the intermediate stage of HAMR, rather than drive the system to the reducing limit. Note that Y₂O₃ is more thermodynamically stable than MgO [12]. The present work is thus unable to

reduce Y_2O_3 , however investigating the effect of the oxide species inclusion on the HAMR reduction was still a motivation of the study.

2. Materials and Methods

2.1. TiO₂ Synthesis

TiO₂ was synthesized via the solvo-thermolysis of Titanium Tetrabutoxide (TBT). To produce 2 g of TiO₂, 8.5 mL of TBT was dissolved in 30 mL of absolute ethanol, then mixed for one hour. Concurrently, a solution was prepared of 4 mL of deionized water, 30 mL of absolute ethanol, 10 mL of glacial acetic acid, and 0.052 g of $Y(NO_3)_3 \cdot 6H_2O$, if doping. The rationale behind the dopant concentration was an intent to create a titanium alloy with 1 wt % Y following a theoretically perfect reduction of TiO₂. The solutions were combined and adjusted to pH 3 with the addition of 3 mL of 2.5 M HNO₃. Maintained at 60 °C, the solution was stirred for two hours, then allowed to rest and age overnight to produce a gel. The gel was dried at 80 °C under a gentle compressed air flow until presenting completely dry, coarse yellow granules. The dried gel was ground and calcined at 500 °C in an ambient atmosphere for two hours.

2.2. HAMR Reduction

3 g of a 1:1:1 mass ratio blend of doped TiO₂, MgCl₂, and Mg metal powder were prepared and loaded into 3 crucibles (1 g per crucible). This process was repeated for the undoped TiO₂. The two blends were reduced simultaneously in separate regions of a tube furnace at 750 °C for four hours. The heating and cooling stages were performed with ramps of 10 °C/min. An Ar gas atmosphere flowing at 50 mL/min was employed in the tube from room temperature to 600 °C, at which point the atmosphere was switched to BOC A5 Forming Gas (95% Ar, 5% H₂) flowing at 50 mL/min. The forming gas atmosphere was maintained until the reduction holding time was complete. During the cooling period, the atmosphere was returned to Ar gas flowing at 50 mL/min.

To wash a powder of interest, 1 g of as-reduced powder was removed from the crucible and placed into a beaker. 10 mL of deionized water was added and the solution was stirred for 10 min before being allowed to settle. The supernatant was removed and the washing was repeated for a total of three washes. The washed powders filtered with a Buchner apparatus (Borosil, Ahmedabad, India), then dried on the filter paper at 80 °C for two hours in a conventional oven.

Powders of interest were resin mounted in Specifix-40 resin (Struers, Cleveland, OH, USA) and cured overnight at 60 °C. The mounted samples were ground, polished with diamond suspensions, and sputter coated with platinum to reduced potential charging effects. Energy-dispersive X-ray spectroscopy (EDS) at% readings were calibrated by analyzing a commercial TiO₂ powder.

2.3. Characterization

XRD was performed on a Rigaku Ultima IV (Rigaku Corporation, Akishima-shi, Japan). SEM imaging and EDS analysis were performed utilizing a Philips XL30 FEG Scanning Electron Microscope (Philips, Eindhoven, The Netherlands). The 'L' emission line was selected for Y, the 'M' emission line was selected for Pt (present as the samples were sputtered to prevent charging effects), and the 'K' emission line was selected for all other elements. Particle size analysis was performed utilizing a Malvern Panalytical Mastersizer 3000 (Malvern Panalytical Ltd., Cambridge, UK).

3. Results

3.1. Reference TiO₂ & EDS Calibration

A spray-dried reference TiO_2 powder was mounted and analyzed via EDS (see Figures 2 and 3). The reference's At% ratio of Ti:O was noted to be 1:1.14, with the EDS system only reporting approximately 57.1% of the expected number of Oxygen atoms for the TiO₂ matrix. Thus, in all subsequent EDS measurements, the EDS readings were



adjusted by dividing the Oxygen At% by 0.571 and renormalizing the elemental readings to sum to 100%. Carbon readings were assumed to originate from the mounting resin.

Figure 2. Cross-section of reference TiO₂ particles, and the yellow frame indicates the area selected for EDS analysis.



Figure 3. EDS elemental spectrum measurement of reference TiO₂ from yellow frame *i* from Figure 2. * oxygen adjusted.

3.2. TiO₂ Powder Characterisation

A challenge presented during the synthesis of the sol-gel TiO_2 powders was that of inconsistent particle size distributions. Such powder inconsistencies may have induced kinetic or surface area related factors to the HAMR reactions that would subsequently mask any kinetic/thermodynamic effects of the Y-dopant species. The particle size distributions of the synthesized TiO_2 particles used in the present work were measured and presented in Figure 4, displaying similar particle size distributions. The particle size distributions



ranged from 300 to 10 μ m, with a mean particle size of approximately 55 μ m. A long tail of fine particles ranged from 250 nm–10 μ m.

Figure 4. Particle Size Analysis of Synthesized TiO₂ Powders.

Phase and crystallite size analysis was performed via XRD. All XRD pattern peaks were matched to Anatase phase TiO₂. The presence of an amorphous 'hump' indicated the presence of amorphous TiO₂. Extensive peak broadening indicated the presence of nanocrystalline grains. The nanocrystalline and amorphous structure was attributed to the low temperature formation process used to synthesize the TiO₂ powders.

To perform crystallite size analysis, the doped and undoped powders were baseline corrected to exclude the amorphous 'hump', peaks were fitted, and calculations were performed on the (101) Anatase peak (the left-most, most intense peak) via the Scherrer equation (see Equation (1))

$$D = \frac{K\lambda}{\beta cos\theta} \tag{1}$$

(*D* = average crystallite size (nm), *K* = constant = 0.89, λ = X-ray diffractometer wavelength = Cu-K α = 0.154 nm, β = full-width half-maximum (radians), θ = diffraction angle (radians)) [10]

XRD analysis was performed before and after calcination of a selected synthesized TiO_2 powder (see Figure 5). As-dried, prior to calcination, the average sol-gel TiO_2 crystallite size was calculated to be 6.7 nm. Following calcination, the average crystallite size was calculated to be 8.4 nm. This indicated the growth of nano-crystalline TiO_2 grains in the synthesized powders following calcination. The reduction in size of the amorphous 'hump' following calcination indicated the ordering of amorphous TiO_2 phases around nanocrystalline grains present in the as-dried powders.

Variations in the XRD baseline level were observed between TiO_2 powders synthesized in different batches, with doped TiO_2 tending to present lower levels of the amorphous 'hump' than undoped TiO_2 , suggesting that the dopant species assisted in the nucleation of nanocrystalline grains from an amorphous, low-temperature TiO_2 phase. No shifted or additional XRD peaks were observed (visually and qualitatively) as a result of Y-doping (see Figure 6). Crystallite size analysis was performed on the powders reduced in the present work, with average crystallite sizes of 8.4 nm for the doped powder and 10.6 nm for the undoped powder.



Figure 5. XRD patterns of synthesized TiO₂ before (blue) and after (red) calcination.



Figure 6. XRD pattern comparison between doped and undoped TiO₂ particles (* feedstocks for reductions presented in present work).

Morphology and cross-section analysis of the synthesized TiO₂ powders was performed via SEM imaging and presented in Figures 7 and 8. Conchoidal facture features were observed, consistent with the fracture of fine-grained materials [13]. The jagged, sharp, and plate-like powder cross-section were consistent with the formation of smaller particles by the conchoidal fracture of larger particles by grinding. The fine tail of the particle size distribution analysis was visually confirmed by the presence of particles <10 μ m. The cross-sections further demonstrated that the interior of the synthesized TiO₂ particles were dense and non-porous. EDS measurements were performed to determine the Ti:O at% ratio of the particles. Following oxygen adjustment, the Ti:O ratios were near 1:2.4 for both doped and undoped sol-gel TiO₂.



Figure 7. SEM image demonstrating conchoidil fracture morphology of TiO₂ Particles.



Figure 8. Cross-sections of doped (**a**) and undoped (**b**) sol-gel TiO₂ particles, and the brown frame *i* and *ii* indicate the areas selected for EDS analysis.

No distinct Y rich phases were observed in doped TiO_2 cross-sections at the magnifications studied. EDS measurements observed slight Y signals in doped powders (0.23 at%, 1.15 wt %, see Figure 9). As doping was performed to produce 1 wt % of elemental Y in a Titanium matrix following a theoretically perfect reduction of TiO_2 , a signal from 0.6 wt % was required in EDS measurements of the sol-gel TiO_2 prior to reduction. Note that Y-levels were reported in the undoped TiO_2 (0.05 at%, 0.25 wt %, see Figure 10); as no Y-species were added to the undoped powder, it was assumed that this reading was in the reach of instrument signal noise, reducing confidence in the doped powder EDS reading mentioned prior.



Figure 9. EDS elemental spectrum measurement of doped, calcined sol-gel TiO₂ yellow area *i* in Figure 8a, (* Oxygen adjusted).



Figure 10. EDS elemental spectrum measurement of undoped, calcined sol-gel TiO₂ yellow area *ii* in Figure 8b. (* Oxygen adjusted).

3.3. Initial Stage HAMR

XRD analysis was performed on the HAMR blend prior to and following initial reduction (see Figure 11). As expected, phase matching identified Mg, Anatase, and Bischofite (MgCl₂•6H₂O) in the precursor blend. The water of hydration in the MgCl₂ salt was noted to be a potential source of Mg consumption, reacting with the metal and leading to the formation of a passivating Mg(OH)₂ film and Hydrogen [14]. No evidence of the formation of Mg(OH)₂ was observed in the XRD analysis of the HAMR blend prior to the reduction. Mg(OH)₂ decomposes to MgO between 300–330 °C [15], and thus could not be observed following HAMR reduction. Following reduction, the crucibles were observed to contain a dense white crust, beneath which was a friable black powder. Note that the Alumina (Al₂O₃) crucibles are less thermodynamically stable than MgO [12], indicating that the crucibles may have been reduced during the experiments. However, no Aluminum-related phases were observed in XRD analysis, and the crucible interiors did not appear to be notably consumed.



Figure 11. XRD Pattern of HAMR Blend Prior to Reduction.

A portion of the white crust was isolated and analyzed via XRD, revealing it to be comprised of MgO. XRD analysis of the washed, reduced powder was presented in Figures 12 and 13. Overall, a significant reduction in Mg metal related peaks was observed, coinciding with the emergence of intense MgO peaks. This indicated forward progress of the HAMR reaction. Two distinct magnesium titanite phases were observed (MgTiO₃ and Mg₂TiO₄), indicating intermediate progress of the reaction. Finally, a hard-to-differentiateby-peak-pattern product phase was observed, attributable to either to the suboxide Ti₂O, or α -Ti(O)—Titanium with dissolved Oxygen in solid solution. No Titanium Hydride phases were observed. Similarly, although expected as a result of the thermal decomposition of Y(NO₃)₃, no Y₂O₃ phases were observed in the XRD analysis [16].



Figure 12. XRD pattern of HAMR Blend Following Reduction.



Figure 13. Selected XRD pattern range from Figure 12.

Observing Figure 13, the height, width, area, and location of the product phase peaks were used as qualitative indicators of the reaction progress. Following reduction, the intermediate phase Qandilite (MgTiO₃) was observed to be less intense in the doped powder than the undoped powder. The product phase peak was observed to be taller and broader in the doped powder than the undoped powder. Together, these observations indicated that the doped powder progressed to a later stage of the HAMR process than the undoped powder for the same reduction parameters. This result indicates a potential kinetic or thermodynamic influence of the dopant species on the HAMR reaction.

The broad nature of the product peaks was attributed to the conversion of nanocrystalline TiO₂ grains, or the formation of a range of non-stoichiometric crystallites with different compositions. Note that α -Ti possesses a considerably large solid solubility rage for O [7].

Significant peak shifting was observed in the doped powder. Further, the product phase peaks were 'stepped', indicating them to be comprised of two phases. The right-most phase was attributed to Ti₂O, while the left-most was attributed to a severely peak-shifted α -Ti phase. A peak associated with the same α -Ti phase, with similar shifting, was observed at 2θ angle of 34° , further demonstrating the severity of the shift.

SEM cross-section analysis was performed on washed powders and presented in Figure 14. Washing was performed to remove hygroscopic MgCl₂ from the samples so as to avoid adverse effects of water ingress on the mounted samples.

The cross-sections generally demonstrated complete interior remodeling of the precursor particles to bright, fine, sponge-like morphologies. EDS measurements demonstrated the ingress of Mg to both doped and undoped particles (see EDS readings Figures 15 and 16, taken from areas displayed in yellow frame ii in the Figure 14a & yellow frame i in the Figure 14c respectively). The presence of Cl signatures in the EDS readings indicated that the preparatory washing was not completely successful in some samples/sample regions. Conspicuously lacking from the particle interiors were features consistent with the literature phase formation mechanism. Specifically, dense cores penetrated by Magnesium Titanite needles were not observed, neither were remodeled shells



migrating towards to particle cores. This was despite strong XRD phase identification of the intermediate phases in the reduced powders.

Figure 14. Cross-sections of partially reduced TiO2 particles; (**a**,**b**), undoped TiO₂ reduced at 750 °C for 4 h, and yellow frame *i* and *ii* indicate the area selected for EDS analysis,(**c**) doped TiO₂ reduced at 750 °C for 4 h, the yellow frame *i* and *ii* indicates the area selected for EDS analysis, and (**d**) doped TiO₂ reduced at 900 °C for 4 h.

Extensive crystal formation in the undoped powder interiors was observed, with EDS measurements of the bright crystals reporting a consistent Mg:O:Ti at% ratio near to 0.3:1.7:1, respectively, normalized to Ti (see EDS reading Figures 17 and 18, taken from yellow frame i in the Figure 14a and yellow frame i in the Figure 14b, respectively). One instance of a similarly bright, dense phase was observed in the cross-sections of the doped powder, however it was not as extensive in interior remodeling or as apparently crystalline (see yellow frame ii in the Figure 14c). EDS measurements of this region presented Mg:O:Ti at% ratios of near 0.3:1.8:1, respectively (normalized to Ti, see EDS measurement, Figure 19). Thus, while of similar composition, this observed phase indicated that Y-doping may have inhibited the formation of the Mg-Ti-O crystals observed in the undoped, reduced TiO₂ matrix, again indicating a kinetic/thermodynamic influence of the dopant species.



Figure 15. EDS reading from yellow frame *ii* in Figure 14a, demonstrating Mg ingress to undoped, reduced TiO₂ particles, * oxygen adjusted.



Figure 16. EDS reading from yellow frame *i* in Figure 14c, demonstrating Mg ingress to doped, reduced TiO₂ particles, * oxygen adjusted.

SEM cross-section analysis further demonstrated the growth of large, blocky MgO crystals on particle surfaces, consistent with the byproduct location in the literature. However, these surface growths were not observed ubiquitously.



Figure 17. EDS measurement of bright crystal—from yellow frame *i* in Figure 14a, * oxygen adjusted.



Figure 18. EDS measurement of bright crystal—from yellow frame *i* in Figure 14b, * oxygen adjusted.

The crystalline appearance of the by-product MgO was qualitatively consistent with sharp, narrow XRD peaks for MgO (sharp peaks generally indicating high crystallinity). For reductions performed at 750 °C, the MgO crystals were observed to be denser than in powders reduced at 900 °C. In the latter, porous networks of MgO crystals were observed to extend up to 50μ m from TiO₂ particle surfaces (see Figure 14d). This observation indicated that the byproduct MgO phase formed particle agglomerating networks with morphologies sensitive to temperature. Mechanistically, the lower temperature reductions—with slower diffusion rates/kinetics—may promote slower, denser crystal growth. In contrast, higher temperature reductions may promote faster, less ordered crystallization of the byproduct phase.



Figure 19. EDS measurement from bright, interior splotches in doped, reduced powder—from yellow frame *ii* in Figure 14c, (* oxygen adjusted).

Note that particle abrasion during the washing procedure likely damaged such MgO sponges. Such abrasion may account for the lack of MgO on some rebuilt particle surfaces. Extensive networks of MgO were hypothesized to be responsible for the friable nature of the powder masses inside the crucibles following reduction.

Trace quantities of β -Titanium were detected in the undoped, reduced powder, indicating that select TiO₂ particles were able to undergo extensive deoxygenation to approach the reduction limit of the Ti-O-Mg system (see Figure 13).

No distinct Y-rich phases or particles were observed at the magnifications studied. Y-levels were assumed to be near to the signal-noise ratio of the EDS measurements. Following the addition of an equal wt % of Mg (subsequently reacting to form byproduct MgO) and the removal by washing of an equal wt % of MgCl₂, the separation of a signal from 0.5 wt % of the sample would have been required to detect Y in EDS measurements of the reduced powders.

HAMR powders reduced at 900 °C for four hours were investigated but not presented extensively in the present work as a result of the production of inconsistent particle size distributions during the feedstock synthesis. However, of note was the presence of another unusual and unexpected microstructure not found in the literature. A bright 'pop-corn' interior remodeling feature was observed inside fine sponge-like cases in these powders once reduced (see Figure 14d). Further discussion of the 900 °C powders is beyond the scope of the present work.

4. Discussion

Nanocrystalline and amorphous materials possess higher bulk diffusion rates as they contain larger volumes of disordered regions. The nano-crystalline/amorphous nature of the TiO₂ synthesized in the present work is proposed to explain the unexpected morphology of the reduced particles.

Fast diffusion agents can improve solute homogenization of a metal. It is hypothesized that the addition of Y species acted as a self-diffusion enhancer for the TiO_2 particles synthesized in the present work. Such kinetic modification may have improved the reduction rate of the reaction.

While it is evident that insufficient magnesium was added to allow the system to reach the 2 wt % dissolved oxygen reducing limit of TiO₂ by Mg, the resulting intermediate reduction stage elucidated differences in the HAMR of TiO₂ as a result of Y-doping.

The absence of titanium-hydride phases from the present analysis was attributed to a de-facto dehydrogenation stage, which was performed by removing the forming-gas atmosphere at the end of the reaction soaking time. As the samples were cooled in the high thermal mass environment of the furnace while under Argon, any hydrogen in the reduced powders would have been driven out of the Ti(O) matrix, as is intentionally done in the HAMR deoxygenation stage, and thus Ti(H) phases would not be present for the following characterization.

Future research directions may aim to reduce nanocrystalline and/or Y-doped TiO₂ at higher temperatures, in larger batches, and/or with larger quantities of Mg. This may allow future work to elucidate whether Y-doped or nanocrystalline feedstocks present advantages when compared to the HAMR of porous or dense, crystalline TiO₂, potentially shortening the reduction process duration.

In the present work, Y-doping was performed at the very beginning of the HAMR process. An alternative doping point is suggested: following the leeching of Reduced powders (from HAMR stage one), during granulation, and prior to sintering of Ti(O)(H) powders, Y-rich dopant species may be incorporated. The Y-species may assist the Deoxygenation stage by capturing Oxygen and producing desirable nano-dispersoids to strengthen the resulting deoxygenated HAMR Ti powders/powder metallurgy parts. Note that the Y-dopant species would be required to maintain reasonable alloying concentrations.

5. Conclusions

The present work investigated the HAMR reaction with TiO_2 feedstocks that varied from bulk-crystal TiO_2 powders presented in the literature. The following conclusions were reached:

- Nanocrystalline TiO₂ powders were synthesized via the solvo-thermolysis of titanium tetrabutoxide. Y-dopant levels in the synthesized TiO₂ were near detection limits for the EDS techniques of the present analysis, however elevated levels of Y were detected in the doped TiO₂ powder.
- The first stage of the HAMR process -Reduction- was partially performed, with XRD
 patterns demonstrating differences in the development of intermediate and product
 phases as a result of rare-earth doping.
- A variety of internal microstructures were observed in reduced powders that did not follow the expected phase evolution of fully dense, highly crystalline TiO₂ particles. This observation was attributed to the nanocrystalline and amorphous structure of TiO₂ feedstock.
- Byproduct MgO phases were observed to grow as porous, particle agglomerating networks, with morphologies sensitive to reduction temperature.
- The use of nanocrystalline and/or rare-earth doped TiO₂ feedstocks was indicated as potential method to improve the reaction kinetics/thermodynamics of the HAMR process.

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