



Regular article

Synthesis of spherical nanocrystalline titanium hydride powder via calciothermic low temperature reduction



Inge Lindemann^{a,*}, Monika Herrich^a, Bernhard Gebel^a, Romy Schmidt^{a,b}, Ulrich Stoock^{a,b}, Margitta Uhlemann^a, Annett Gebert^a

^a IFW Dresden, P.O. Box 270116, D-01171 Dresden, Germany

^b TU Dresden, Institute of Materials Science, Helmholtzstraße 7, D-01069 Dresden, Germany

ARTICLE INFO

Article history:

Received 22 July 2016

Received in revised form 15 November 2016

Accepted 16 November 2016

Available online xxxx

Keywords:

Titanium

Hydrogen

Mechanical milling

Nanocrystalline materials

X-ray diffraction

ABSTRACT

Spherical nanocrystalline TiH₂ powder was synthesized by calciothermic reduction of TiO₂ with CaH₂ at low temperature. Reduction was performed in solid state either by reactive milling in H₂ or via pre-milling in Ar with subsequent heat treatment in H₂. Reactively milled powders are pyrophoric on exposure to air. Leaching of the side product CaO was only successful from the pre-milled and heat treated powders. As synthesized TiH₂ is stable in air and desorbs H₂ below 600 °C forming nanocrystalline Ti. Therefore it is suitable to prepare ultra finegrained cp-Ti.

© 2016 Acta Materialia Inc. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Titanium alloys are suitable for a variety of advanced applications due to an exceptional set of properties including low density, high specific strength, corrosion resistance and biocompatibility [1]. Strength and wear resistance of cp-Ti need to be increased with regard to biomedical applications. This can be achieved by grain refinement according to the Hall-Petch relationship [2]. Up to now, mainly the aerospace alloy Ti6Al4V is used for implants due to its higher strength [3]. Conventionally, titanium is produced by the conversion of TiO₂ following the expensive batch process developed by Kroll. Titanium sponge is made from TiO₂ via synthesis of TiCl₄ and its subsequent reduction with Mg melt. The sponge is homogenized and leached for final parts production from purified ingots. Hard workability further increases the manufacturing cost [4]. The price of titanium and its alloys limit their usage in many fields [5]. At least cost of workability can be lowered by powder metallurgical processes and new near-net shape methods. But the price of good quality powder is high. Powder is produced either by gas atomization (spherical, >10 μm particle size) or via the hydride-dehydride method (angular) [6]. Therein hydrogenation of the sponge results in brittle TiH₂ which is crushed and subsequently dehydrogenated by vacuum annealing. Recently, sintering of TiH₂ instead of Ti showed reduced oxygen content due to surface cleaning effect [7,8]. Moreover higher densification was achieved using TiH₂ due to reduced cold welding and friction during the compaction process

[9]. Most importantly, TiH₂ is stable in air up to 150 °C whereas Ti powder is extremely reactive [10,11].

Along with many alternative approaches the Metal-Hydride-Reduction process (MHR) is one promising option for Ti powder synthesis [12]. Therein TiO₂ is reduced with CaH₂ at 1100–1200 °C, well above the melting point of Ca (T_m = 840 °C). Excess of CaH₂ (50%) is needed due to high vapor pressure of Ca. Particle size of the as-synthesized Ti is in the micron range with a spongy morphology [10]. A similar synthesis of TiH₂ by reduction of TiO₂ with CaH₂ (50% excess) above the melting point of Ca was already conducted by Alexander in 1947 [13]. Ephraim and Patel [14] published the solid-solid transformation of TiO₂ during the reduction with Ca but at temperatures between 850 °C and 950 °C where Ca should be liquid. Additionally the preform reduction process was proposed for reduction of TiO₂ [15] or Ti ores [16] with Ca at 1000 °C. CaH₂ is the preferable reducing agent for synthesis of titanium hydride [17]. The reduction temperature can be lowered by mechanochemical processing of the starting materials [18]. Froes et al. [19] prepared TiH₂ by reactive milling of TiO₂ and CaH₂ in Ar atmosphere which resulted only in limited conversion [19]. They have continued their studies based on a synthesis route starting from titanium chlorides [20]. Davids et al. [21] prepared TiFe from ilmenite using CaH₂ in a two-step process. However, hydrogen capacity of the metal-hydride forming alloy was only 0.5 wt.% which is significantly lower than the expected value of 1.8 wt.% H₂.

This letter highlights the low temperature synthesis of spherical nanocrystalline TiH₂ powder by reduction of nanocrystalline TiO₂ in anatase modification TiH₂ with CaH₂ in stoichiometric ratio. Two approaches

* Corresponding author at: IFW Dresden, Institute for Complex Materials, P.O. Box 27 01 16, D-01171 Dresden, Germany.

E-mail address: I.Lindemann@ifw-dresden.de (I. Lindemann).

for TiH_2 synthesis are investigated, on the one hand pre-milling in Ar with subsequent low temperature heat treatment in H_2 and on the other hand reactive milling of the reagents in H_2 . Especially the effect of pre-milling on the reduction reaction is elucidated.

TiO_2 (>99%, –325 mesh, anatase) and CaH_2 (99.99%) powders were purchased from Sigma Aldrich as reagents. Milling was carried out using a Fritsch planetary ball mill P6 (sun disc $r = 0.0608$ m) with a 220 ml stainless steel (SS) vial (Evico Magnetics) with 37 SS-balls (\varnothing 10 mm) and a ball to powder ratio of 40:1. The starting materials were mixed in stoichiometric ratio 1:2 of TiO_2 and CaH_2 . In the first approach pre-milling was done with 200 rpm in 1 bar Ar for 1 h, 2 h, 10 h and 15 h. Reduction was performed during subsequent heat treatment in static H_2 atmosphere ($p_{\text{start}} = 0.2$ bar) up to 750 °C (5 K min^{-1}) without dwell using Al_2O_3 crucible inside a quartz glass tube. A reference sample was prepared by homogenization of the starting materials with a Retsch Shaker Mill MM200 with 25 Hz for 3 min (10 ml SS-vial, 1 SS-ball \varnothing 10 mm). Reduction temperature for the shaken reference sample was increased to 800 °C (5 K min^{-1}) with 2 h dwell. In the second approach reactive milling in 1 bar H_2 was carried out with 500 rpm in the Fritsch P6. For XRD analysis powders were filled into 0.7 mm capillaries and sealed. Patterns were collected at a STOE Stadi diffractometer with $\text{MoK}\alpha_1$ radiation ($\lambda = 0.70926$ nm). Differential scanning calorimetry and thermogravimetry (DSC-TG) was carried out simultaneously using a Sensys evo (Setaram) mounted inside an Ar-filled glovebox coupled with a Pfeiffer vacuum mass spectrometer (MS, Omnistar) outside the glovebox. H_2 desorption was monitored with the integrated C-SEM detector. Entire sample handling and transfer was done in Ar atmosphere (H_2O , $\text{O}_2 < 2$ ppm). After reduction all powders were exposed to air for the first time to remove the oxidic calcium species. Foremost, they were stirred in water and subsequently treated with dilute acetic acid (10%). Then TiH_2 was percolated from the solution using a ROBU glas frit followed by washing with lots of deionized water and finally ethanol. TiH_2 powder was dried at 50 °C for 24 h in a drying cabinet. SEM analysis was conducted with a LEO FE-SEM (5 kV, InLens). Ca-content was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-OES with an IRIS Intrepid II XUV from Thermo Fischer Scientific GmbH). Furthermore, hydrogen content was measured with an EMGA 621 W (HORIBA) and particle size distribution was examined by a S3500 Particle Size Analyzer (Microtrac) in 1 wt.% SDS (sodium dodecyl sulfate) solution.

The calciothermic reduction of TiO_2 with CaH_2 in the solid state is kinetically hindered by slow diffusion of ions. Therefore ball milling of the reactants in the stoichiometric ratio 1:2 was carried out for mechanical activation. Low energy milling with 200 rpm in Ar results in particle size reduction and grain refinement. XRD patterns after milling the reactants in a planetary ball mill for 1 h, 2 h, 10 h and 15 h are shown in Fig. 1(a). TiO_2 is present in the less stable anatase modification which increases the driving force for the reduction reaction. Reflection peaks of TiO_2 and CaH_2 are broadened in comparison to the shaken reference sample (S) due to reduced grain size and strain induced by milling. The color of the powder changes from white (S) to blueish gray due to surface oxygen vacancies of the TiO_2 . High energy milling with 500 rpm in H_2 is able to start the reduction of TiO_2 with CaH_2 during the milling process. Hydrogen backpressure was applied in order to avoid H_2 desorption from the reaction product TiH_2 according to reaction (2). 1 bar H_2 was chosen for practical reasons as it is well above the theoretical value of the equilibrium pressure and high enough to avoid leakage. The XRD patterns after reactive milling for 2 h and 4 h are also shown in Fig. 1(a). After 2 h there is still some starting material present but after 4 h there is only TiH_2 and CaO left. Therefore we have observed complete conversion of the reaction (1) during milling with high energy. The color of the powder changes from white (reference sample S) to black for both reactively milled samples.

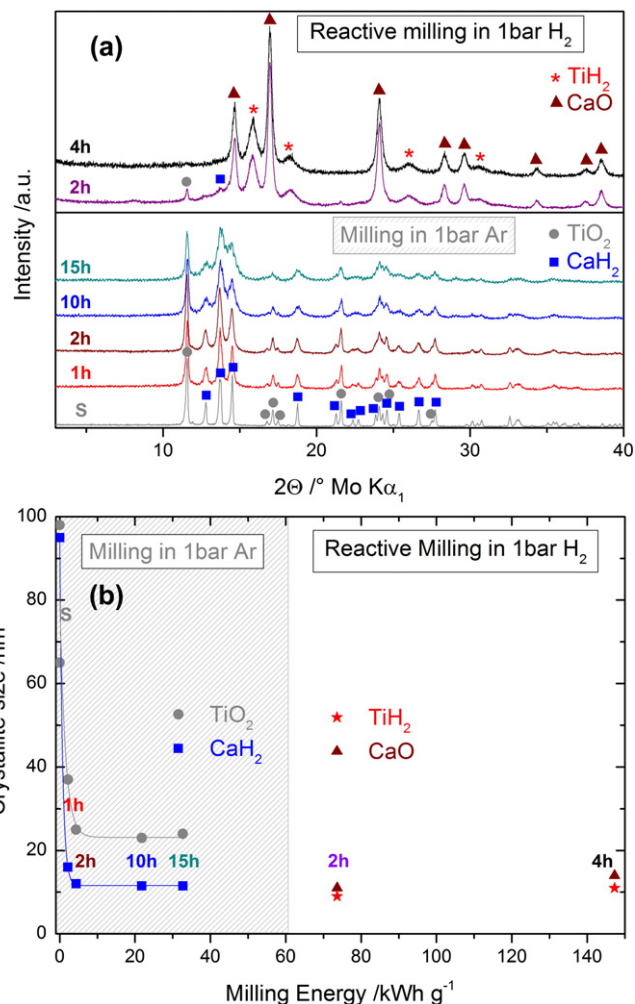
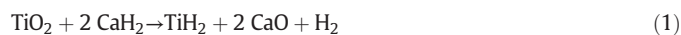


Fig. 1. (a) XRD patterns of millings in 1 bar Ar for 1 h, 2 h, 10 h, 15 h and reactive milling in 1 bar H_2 for 2 h and 4 h in comparison to the shaken reference sample S. (b) Crystallite size calculated by Rietveld refinement vs. milling energy.



Nanocrystalline TiH_2 is obtained in fluorite type (CaF_2) crystal structure with a lattice parameter of $a = 4.455$ Å. Reflections of the products TiH_2 and CaO are broadened due to extremely small grain size and lattice strain. Rietveld refinement (FullProf) was conducted to estimate crystallite size, strain and phase fractions. Crystallite size and strain were assumed to be uniform in all crystallographic directions. Fig. 1 (b) shows crystallite size for all millings (in Ar and H_2) as a function of milling energy. In contrast to milling time it includes the different rotational speeds (ω_p) used in the two milling regimes. Milling energy was calculated according to the collision model published by Burgio et al. [22] using the geometrical parameters of the monomill P6 given by the radius of the plate of the mill ($R_p = 0.0608$ m) and the rotation ratio of plate and vial 1:–1.82. Therein energy impact of one ball per hit ΔE_b was estimated ($K_a = 1$ for inelastic collision, $K_b = 0.98$ for a planetary mill, $m_b = 4.2$ g for one SS ball).

$$\Delta E_b = \frac{1}{2} \cdot K_a \cdot K_b^2 \cdot m_b \cdot \omega_p^2 \cdot R_p^2 \quad (3)$$

Taking into account the collision frequency of one ball $f_b = 4.23\omega_p$, filling factor φ_b ($\varphi_b = 1$ for fillings <30%) and the total number of

Download English Version:

<https://daneshyari.com/en/article/5443509>

Download Persian Version:

<https://daneshyari.com/article/5443509>

[Daneshyari.com](https://daneshyari.com)