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Synthesis of nanopowders of titanium compounds via Flow-Levitation method and study their properties

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Abstract. Nanopowders of titanium compounds TiH₂ and TiC are synthesized via Flow-Levitation method using *in situ* reaction of nascent titanium nanoparticles with the proper reactants. The influence of manufacturing parameters on the composition and the internal structure of the synthesized nanoparticles is examined. Study of TiH₂ nanoparticles using thermal methods revealed hydrogen evolution within the narrow temperature range (390₀-510₀ C), while hydrogen evolution temperature of the commercial samples is higher than 500₀ C.

1. Introduction

Titanium compounds are widely used in various fields of science and technology. Titanium hydride is known as a source of hydrogen gas in manufacturing of porous metal materials, specially aluminum foams [1,2]. It is also used as material for storage, transport and recovery of hydrogen in power engineering applications [3,4]. Titanium carbide is a hard, refractory, abrasion, chemical inert material, which is used as a component of heat-resistant hard alloys, carbidized steels, reinforced alloys, abrasive materials, coatings for cutting tools, etc. [5]. Titanium carbide may be used for metal processing as an alternative to expensive tungsten. The study of physical, chemical and other properties of nanoparticulate titanium compounds is of scientific and practical interest. It is expected that due to higher specific surface area, the properties of nanoparticulate titanium compounds are different from those of “coarse” powders of the same materials. This work is devoted to study of physicochemical properties of nanoparticulate titanium hydride and titanium carbide synthesized via Guen-Miller Flow-Levitation (FL) method invented and developed at the Institute for Energy Problems of Chemical Physics of the Russian Academy of Sciences [6].

2. Experimental

2.1. Method and materials

Figure 1 illustrates the main elements of the apparatus for synthesizing of nanoparticles via the Guen-Miller FL-method. A molten titanium drop levitates inside a high frequency (440 kHz) electromagnetic field produced by a countercurrent inductor coiled around the wall of a cylindrical quartz reactor of 14-15 mm inner diameter. The inductor heats up the metal ensuring its steady



evaporation. The mass lost by evaporation is continuously replenished by metal wire fed into the drop at a preset rate. An inert gas (Ar) input through the main inlet flows steadily from the top of the reactor over the levitating molten drop sweeping the metal vapor downstream. Metal vapor condenses homogeneously into nanoparticles in Zone 1. Nascent nanoparticles flow to Zone 2 where they react with gaseous reactant injected into the reactor through the main or the special inlet at a preset rate. The resulting nanoparticles of titanium compound continue to flow to Zone 3 where they are cooled down, and subsequently collected on a filter at room temperature.

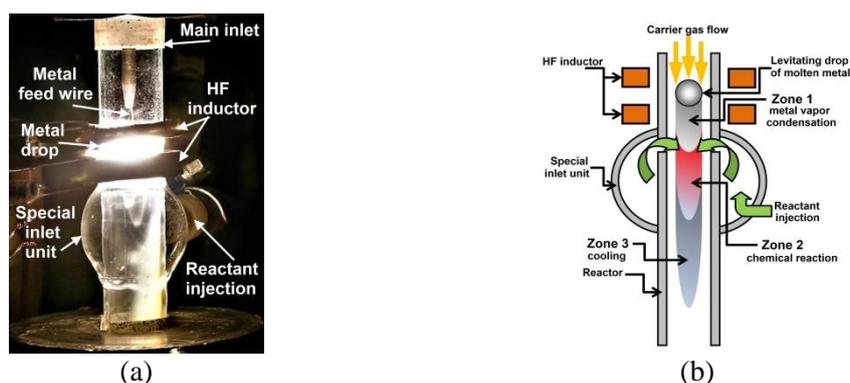


Figure 1. Appearance of the reactor in action (a) and a scheme of the synthesis process (b).

On completion of the synthesis process, nanoparticles of titanium compound were passivated *in situ* by pumping out the inert gas from the apparatus and slowly filling it with atmospheric air (~10-20 h) in order to form a protective titanium oxide layer on the surface of nanoparticles.

2.1.1. Synthesis of titanium hydride nanoparticles. Titanium hydride nanoparticles were obtained via direct interaction of titanium with hydrogen gas [7,8]. Hydrogen can be admixed to the inert gas from the top or injected through the special inlet directly into Zone 2. At this stage, the temperature of the flowing nascent titanium nanoparticles is sufficiently high (400-500 °C) as to secure the stoichiometric reaction: $\text{Ti} + \text{H}_2 = \text{TiH}_2$. Subsequently, the fast motion of the flow to a colder Zone 3 prevents the thermal decomposition of the synthesized TiH_2 particles.

The method allows synthesis of customized “core-shell” nanoparticles under highly controllable conditions. Depending on the manufacturing parameters, it is possible to synthesize nanoparticles of different composition, from pure stoichiometric titanium hydride TiH_2 to mixed composition such as TiH_2 -Ti. One of the main factors determining the composition of the synthesized titanium hydride nanoparticles is the hydrogen concentration in the reaction zone. In the present work, it is demonstrated by the examples of samples TH-1 and TH-2 synthesized at different hydrogen concentrations achieved using different gas inlets (Table 1).

Table 1. Manufacturing parameters and characteristics of titanium hydride nanopowders

Sample	Feed wire rate (g/h)	Ar gas pressure (at.)	Hydrogen gas flow rate (Nl/min)	Hydrogen gas inlet	Crystal phase content (w.%)	Mean size (nm)
TH-1	1.37	0.2	0.125	special design (reaction zone)	TiH_2 – 100	25
TH-2	2.25	0.2	0.125	main (top)	TiH_2 – 94.2 α -Ti – 5.8	30

Synthesized titanium hydride nanopowder is a loose material of black color. The powder, if not properly passivated, is extremely pyrophoric and needs to be handled in an inert atmosphere with decreased oxygen and moisture content. For the present study, the synthesized samples of titanium hydride were subjected to a suitable process of passivation in order to form a protective titanium oxide layer on the surface of nanoparticles which prevents sudden ignition in atmospheric air.

2.1.2. Synthesis of titanium carbide nanoparticles. Titanium carbide nanoparticles were obtained via interaction of titanium in nascent nanoparticles with carbonic reactant gases [9]. In the present work, hydrocarbons such as acetylene (C_2H_2), methane (CH_4) and mixture of propane (C_3H_8) and butane (C_4H_{10}) were used as gaseous reactants. The reactants were injected in the reactor through the adjustable inlet of special design, which location determines Zone 2, depending on the required temperature of the reaction of titanium with the chosen hydrocarbon: $Ti + C_xH_y \rightarrow TiC, TiH_2, C + H_2$.

The reaction conditions and a type of hydrocarbon used determine the composition of the resulting nanopowder. It is possible to synthesize pure crystalline TiC nanoparticles (with small amount of crystalline carbon), as well as nanoparticles of mixed composition such as TiC+TiH₂, TiC+Ti. In the present work, it is demonstrated by the examples of samples TC-1, TC-2, TC-3 (Table 2).

Table 2. Manufacturing parameters and characteristics of titanium carbide nanopowders

Sample	Ar gas pressure (at.)	Ar gas flow rate (m ³ /h)	Reactant gas (hydrocarbon)	Reactant gas flow rate (m ³ /h)	Crystal phase content (w.%)	Mean size (nm)
TC-1	0.2	0.15	C_2H_2	0.15	TiC – 95,2 C – 4,8	21
TC-2	0.24	0.15	CH_4	$3.6 \cdot 10^{-3}$	TiC – 62,9 TiH ₂ – 37,1	27
TC-3	0.5	0.25	$C_3H_8 + C_4H_{10}$	$4.4 \cdot 10^{-2}$	TiC – 86,6 Ti – 13,4	26

Synthesized titanium carbide nanopowder is a loose inert material of black color. However, the synthesized nanopowder of mixed composition can exhibit pyrophoric properties, depending on the content of titanium hydride or residual titanium metal.

3. Results and discussion

3.1. Titanium hydride

Characterization of the titanium hydride nanoparticles was performed via complex of methods of transmission electron microscopy (TEM/HRTEM/EDA/EDX), X-Ray diffraction (XRD), thermal analysis (TGA/DTA/DSC/MS).

X-ray diffraction patterns of titanium hydride samples TH-1 and TH-2 synthesized under conditions indicated in Table 1 are shown in Figure 2.

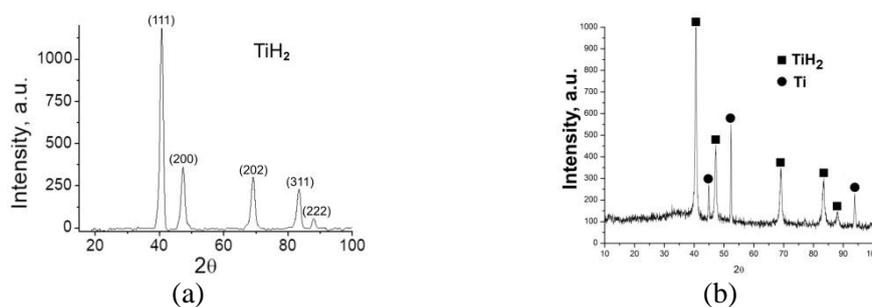


Figure 2. X-ray diffraction patterns of titanium hydride samples TH-1 (a) and TH-2 (b)

The fact that XRD analysis revealed no crystalline phase of titanium oxide formed on the surface of nanoparticles during passivation indicates its amorphous state.

Typical TEM/HRTEM images of samples TH-1 and TH-2 are shown in figure 3 and figure 4, respectively. TEM study of samples TH-1 and TH-2 revealed non-agglomerated arrays of particles of various sizes. The diameters of particles in both samples measured from TEM images ranged from 5 nm to 70 nm (nanoparticles mean size is presented in Table 1). The TEM/HRTEM examination of nanoparticles revealed that the structure of the particles depends on their size. Generally, the smallest particles of the array (up to about 10 nm) look equiaxial and homogeneous, while larger particles

exhibit a core-shell structure with a pronounced faceted shape. Amplified views of HRTEM images expose lattice fringes corresponding to the atomic (inter-planar) spacing. These lattice fringes are found only on the images of the particle cores, and the measured magnitude of the inter-planar spacing $d \approx 0.26$ nm corresponds to the (111) plane of TiH_2 lattice (Figure 3 (b) - inset). No signs of crystallinity of the particle shells (such as lattice fringes, moiré patterns) are observed on the HRTEM images of both samples, which is consistent with the results of XRD analysis. Measurements of shell thicknesses of the HRTEM images of about 20 nanoparticles ranged between 3.5-5.0 nm.

Results of electron diffraction analysis of sample TH-1 and TH-2 are consistent with XRD data.

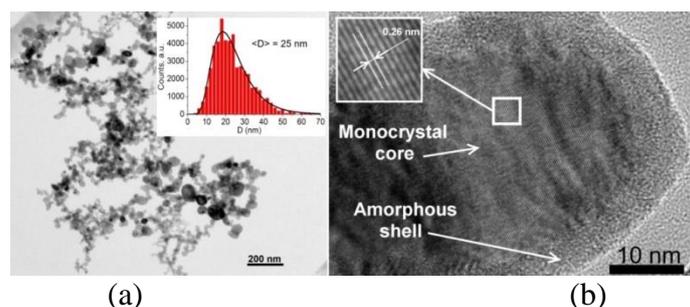


Figure 3. TEM image of sample TH-1 where the inset is the particles size distribution histogram (a) and HRTEM image of an individual particle of the same sample where the inset is the enlarged view of the selected area (b).

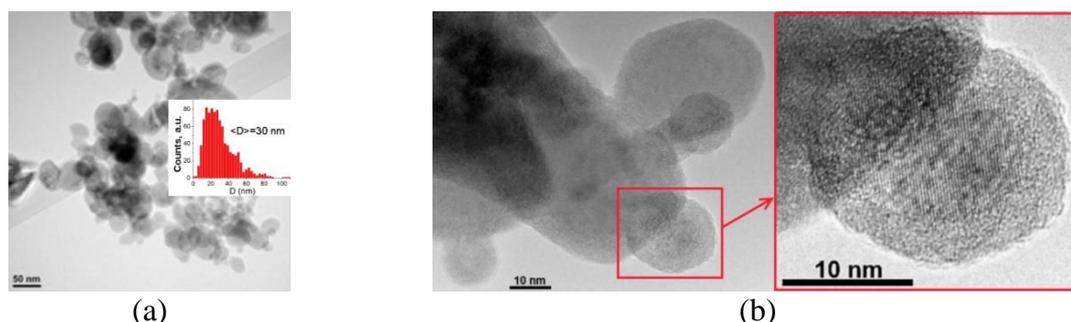


Figure 4. Typical TEM image of sample TH-2 where the inset is the particles size distribution histogram (a) and HRTEM image of the same sample where the enlarged view of the selected particle is shown (b).

Hydrogen release from TiH_2 nanoparticles was studied using thermal methods of analysis. Decomposition behavior of the synthesized sample TH-1 of TiH_2 nanopowder (NP) and commercial titanium hydride powders as the references were studied using simultaneous TG-DTA/DSC and MS analysis. Reference Ref1 is a commercial titanium hydride powder with particle mean size $\langle D_1 \rangle \approx 15$ μm , and reference Ref2 is a coarse titanium hydride powder of particle size $\langle D_2 \rangle \approx 0.5$ mm.

The studies were conducted in high-purity helium gas flow (40 ml/min) at heating rate of 10 $^\circ\text{C}/\text{min}$ within the temperature range of 50-700 $^\circ\text{C}$. TG/DSC analysis of all samples included two successive heating cycles for each sample with no exposure to air during the intermediate cooling. Typical results are shown in Figure 5.

It is evident from the data presented, that a significant feature of TiH_2 nanopowder synthesized via the Guen-Miller FL method is the hydrogen evolution within the narrow temperature range (390-510 $^\circ\text{C}$), which contrasts markedly with commercial samples of larger particle size (with a typical temperature of hydrogen evolution higher than 500 $^\circ\text{C}$). It is also evident that the TiH_2 NP requires less energy to start the decomposition process and that the diffusion of hydrogen is faster in smaller particles than in larger particles.

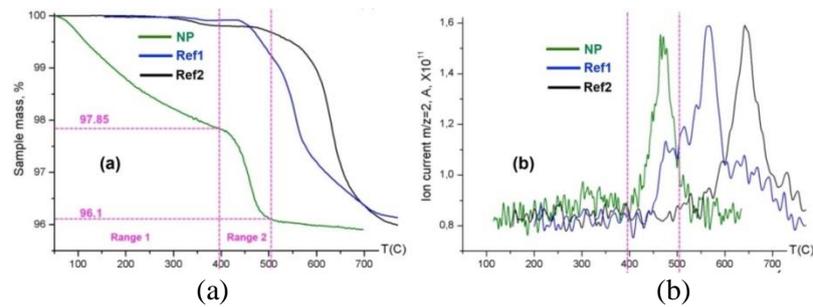


Figure 5. Results of TG-DTA/DSC-MS during the heating cycle showing mass loss of titanium hydride (a) and hydrogen release intensity (b), where NP is synthesized TiH_2 nanopowder, Ref1 and Ref2 are commercial titanium hydride powders.

3.2. Titanium carbide

Characterization of the titanium carbide nanoparticles was performed via complex of methods of scanning and transmission electron microscopy (SEM/TEM/HRTEM/EDX) and X-Ray diffraction.

X-ray diffraction patterns of titanium carbide samples TC-1, TC-2 and TC-3 synthesized under conditions indicated in Table 2 are shown in Figure 6.

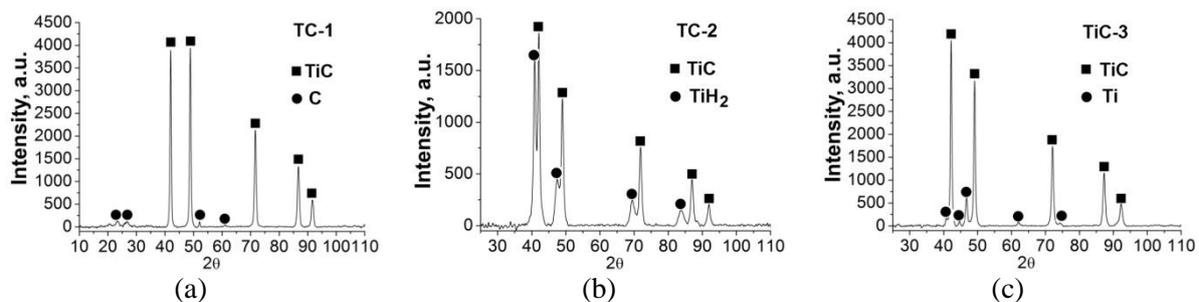


Figure 6. X-ray diffraction patterns of titanium carbide samples TC-1 (a), TC-2 (b) and TC-3 (c)

SEM and TEM analysis of titanium carbide samples revealed close similarity of nanoparticles morphology (Figure 7). All particles, irrespectively of the manufacturing conditions, exhibit equiaxial faceted shape. It is evident from SEM study that nanoparticles are equiaxial polyhedrons. Mean size of particles of all studied titanium carbide samples do not exceed 30 nm.

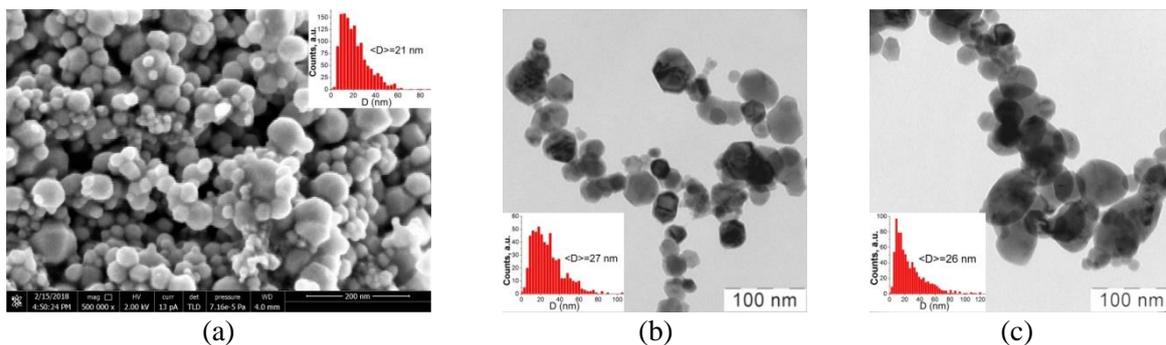


Figure 7. Typical SEM image of sample TC-1 (a) and TEM images of samples TC-2 (b) and TC-3 (c). Insets are the particles size distribution histograms.

HRTEM examination revealed a difference in the internal structure of titanium carbide nanoparticles synthesized under different conditions. Examples are shown in Figure 8. Nanoparticles of the sample TC-1 are pure titanium carbide monocrystals, the measured magnitude of the inter-planar spacing $d \approx 0.251 \text{ nm}$ corresponds to the (111) plane of TiC lattice (Figure 8 (a) - inset). Nanoparticles of the sample TC-2 exhibit the evident core-shell structure, where the shell thickness is about 2.6-2.7 nm. The measured magnitudes of inter-planar spacings at the image of the core

correspond to the (111) planes of TiC ($d \approx 0.251$ nm) and TiH₂ ($d \approx 0.265$ nm) which shows complex crystalline composition of nanoparticles core (Figure 8 (b) - insets). The shell presence can be attributed to formation amorphous titanium oxide layer, as a result of TiH₂ oxidation during the passivation process.

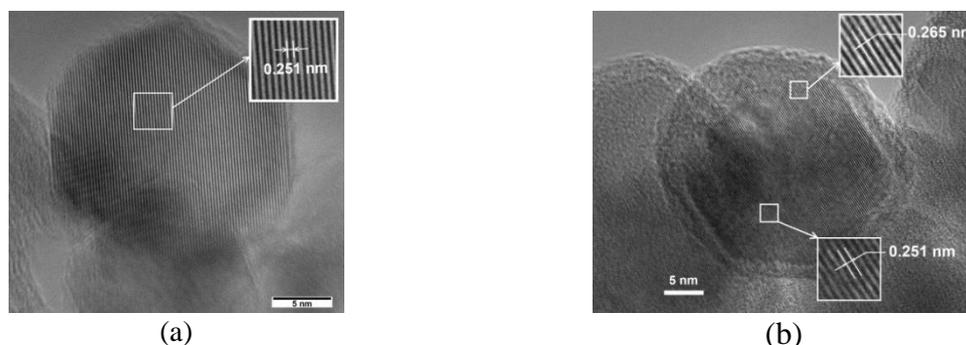


Figure 8. HRTEM images of nanoparticles of the samples TC-1 (a) and TC-2 (b), where the insets are the enlarged views of the selected areas.

4. Conclusion

The results obtained demonstrate the capability of Flow-Levitation method for synthesis of nanoparticles of titanium compounds of customized composition with mean size of less than 30 nm.

Titanium hydride nanoparticles exhibit core-shell structure and possess the promising characteristics for hydrogen recovery as compared to coarse-grained commercial powders.

Titanium carbide nanoparticles characterization displayed the relation between their composition and internal structure. Pure TiC nanoparticles are monocrystalline polyhedrons, whereas nanoparticles of complex composition exhibit core-shell structure.

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