



## Exploring enhanced reactivity of nanosized titanium toward oxidation

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### ABSTRACT

Oxidation of nanosized titanium (nano-Ti), a promising component of energetic compounds, was studied using thermogravimetry and differential scanning calorimetry. To obtain more comprehensive insight into the kinetics and mechanism of oxidation, a variety of complementary non-isothermal and isothermal thermoanalytical experiments were performed. In sharp contrast to micron-sized titanium, oxidation of nano-Ti commences at much lower temperatures (150 °C instead of 650 °C) with profoundly lower activation energies ( $152 \pm 3 \text{ kJ mol}^{-1}$  and  $220 \pm 3 \text{ kJ mol}^{-1}$ , respectively). Moreover, reaction kinetics for nano-Ti obeys the logarithmic law, while in the case of micron-sized Ti kinetics is described by the 2D-diffusion model. At the microscopic level, the observed kinetics of nano-Ti oxidation is explained by switching of the limiting reaction stage to short-circuit diffusion of oxygen through the titanium oxide. This process is promoted by the increase of porosity upon initial water loss and the blocking of pores in the course of oxidation. The kinetic model proposed for oxidation of nano-Ti was independently benchmarked against the isothermal kinetics (zero heating rate limit) and ignition data (high heating rates). Our model provides reliable kinetics of the nano-Ti oxidation, which is valid for both storage and application conditions.

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### 1. Introduction

Nanosized metals and their oxides are promising components of energetic and propulsion compounds [1,2]. They are indeed superior to the micron-sized additives due to more efficient tailoring of the combustion parameters (e.g., increase of the burning rate) [3–6]. However, applications of nanosized metals are hindered by ageing during storage and lack of theoretical understanding necessary for maximizing the energy input of the compositions. Kinetics and mechanism of oxidation are crucial for tackling of both these factors. Unfortunately, the comprehensive models of nanoparticle oxidation are still lacking with only few exceptions [7–10].

Titanium has important applications in the field of energetic materials, in particular, as a component of pyrotechnic compositions [11]. However, the titanium oxidation was mostly studied for simple model systems, i.e., thin films and micron-thickness coatings [12–14], or micron-sized powders [15,16]. Figure 1 summarizes existing information on kinetics of titanium oxidation in a wide temperature range. Below 350 °C the kinetic model of Ti oxidation (the so-called “oxidation law”) is generally supposed to be

logarithmic [17–19]:

$$\alpha(t) = B \ln(t/\tau + 1) + C, \quad (1)$$

where  $\alpha$  is a conversion degree, and  $B$ ,  $\tau$ , and  $C$  are the empirical constants. Note that other models were also proposed to describe the low-temperature oxidation: e.g., the modified parabolic [20] and inverse logarithmic models [21]. Apart from being merely empirical matches to experimental data, these models also represent the underlying physical assumptions. E.g., the inverse logarithmic law is in line with the Cabrera and Mott theory of ion transfer through oxide [22], the power law corresponds to the diffusion in powders with fractal geometry [23], and asymptotic and logarithmic laws refer to self-blocking in porous oxides [24].

At higher temperatures (600–800 °C, Fig. 1), the most important processes leading to the oxide growth are oxygen diffusion to the oxide layer [25], diffusion of titanium cations to the oxide [26], and oxygen dissolution in titanium [25]. In accordance with the Wagner theory, the kinetics in this temperature region obeys the parabolic law, which corresponds to diffusion through the oxide layer driven by the gradient of chemical potential [27]. Finally, the dense oxide scale at higher temperatures (around 1000 °C) begins to disintegrate enabling the oxygen transport to the metal-oxide interface. In this case, kinetics obeys the linear oxidation law, i.e.

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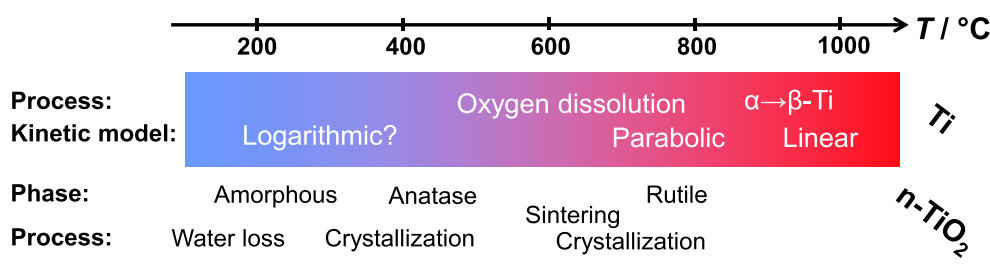


Fig. 1. Schematic of kinetics and mechanism of titanium oxidation in the wide temperature range ( $\sim 100$ – $1000$  °C) based on literature data for micron-sized Ti. Also the additional overlapping processes, complicating the oxidation, are presented for titanium and nanosized titanium dioxide (the most abundant product of nano-Ti oxidation).

the process is dominated by the gas supply for the boundary reaction [14].

In contrast with above discussed issues, very little is known on the thermal behavior of *nano-sized* Ti powder. Recently, Zachariah and co-workers [28] have reported for the first time the ignition kinetics of nano-Ti particles at relatively high temperatures (1700–2500 K). The extremely low activation energy value obtained,  $53 \text{ kJ mol}^{-1}$ , is comparable to those reported for aluminum ( $25$ – $32 \text{ kJ mol}^{-1}$ ) [29] and boron ( $33 \text{ kJ mol}^{-1}$ ) [30] nanoparticles. However, the general reasons for such low activation energies remain poorly understood.

Recent advances in thermal analysis [31–33] were implemented in a number of reliable thermokinetic tools meant for study of kinetics of solid-state reactions over a broad range of temperatures. In the present contribution, we aim at application of these techniques to study the kinetics of nanosized titanium oxidation using the non-isothermal experimental data. The proposed kinetic model was independently benchmarked against direct experimental data from isothermal ageing and ignition experiments. These results give mechanistic insight into primary stages of nano-titanium oxidation and yield the reliable kinetic parameters for this process at the nano scale.

## 2. Experimental

### 2.1. Synthesis

The titanium nanopowder was synthesized via flow-levitation method using MIGEN equipment based on Gen-Miller technique [34]. The molten titanium droplet was suspended in the field of high-frequency (440 kHz) counter-current inductor inside the quartz tube (inner diameter about 14 mm) under a flow of argon. The drop was heated by the field of the inductor up to the temperature ca. 2200–2300 °C, which is sufficient for substantial evaporation to occur. Titanium vapor condense homogeneously in a cold inert gas, thus forming the nanopowder aerosol, cooled and trapped with a filter downstream. The Ti wire was fed continuously to sustain the process (photography of a setup is shown in Fig. S1, Supplementary Material). Titanium powder in a fine state is liable to ignite spontaneously on exposure to air [35,36], thus the nano-Ti has to be passivated prior to handling. Stabilization of the nano-Ti was performed by slow in-leakage of argon-oxygen mixture.

### 2.2. Methods

Morphology of the powders studied was visualized with scanning electron microscope Helios NanoLab<sup>TM</sup> 660 (FEI). Nano-sized titanium was also studied with the transition electron microscopy TECNAI<sup>TM</sup> G<sup>2</sup> F20 TMP (FEI) supplemented by local elemental analysis. Particle-size distribution for nano-Ti powder revealed by analysis more than 1500 particles from the TEM images.

The specific surface area (BET) values were determined with FlowSorb III 2305 (Micromeritics) by the measuring adsorption of gas mixture (30% N<sub>2</sub>/70% He) on the powder. X-Ray diffraction patterns were obtained using diffractometer ADP-1 (Russia) with Co-K $\alpha$  radiation.

The oxidation of titanium samples was investigated with STA449 F3 (Netzsch) thermal analyzer under linear heating conditions from room temperature. Measurements were performed in air flow ( $100 \text{ ml min}^{-1}$ ) with argon flowing ( $20 \text{ ml min}^{-1}$ ) through the balance system. The samples of 5–6 mg were loaded in open alumina pans. Differential scanning calorimetry (DSC) and thermogravimetry (TGA) signals were registered simultaneously at heating rates of 0.5, 1, 2, 5, 10 and  $20 \text{ K min}^{-1}$ . Preliminary calibrations of temperature and heat flow signals were performed according to manufacturer recommendations for each heating rate.

Thermogravimetric isothermal data were acquired according to the following program: (a) heating to 120 °C in the argon flow, (b) isotherm during 15 min, (c) changing of the gas to air flow and 15 min wait for equilibration, (c) heating with rate  $10 \text{ K min}^{-1}$  to the selected temperature, (d) the isothermal segment. The sample mass of 5 mg, which is similar to non-isothermal runs, was used. After the isothermal run with nano-Ti, the blank measurement was conducted with the nano-TiO<sub>2</sub> (produced by the complete oxidation of the nano-metal). Finally, the TGA data for the blank run was subtracted from the experiment with titanium sample. The resulting data comprise the (conversion degree) vs. (time) points after the exclusion of the heat-up and temperature equilibration periods. Accordingly, the conversion degree was counted to be zero at the beginning of the isothermal segment.

### 2.3. Kinetic analysis

Calculations of the kinetic parameters from the experimental TGA data were performed using the THINKS program [37] according to the ICTAC recommendations [38]. In present study we use several routines from THINKS package: (a) exclusion of runs with self-heating (in accordance with the procedure of Farjas and co-workers [39]); (b) differential isoconversional Friedman analysis [40] for the evaluation of the activation energy variation during the oxidation; (c) combined kinetic approach to single-step processes [33] along with the reduced master plot technique [41] to identify the reaction type; (d) nonlinear regression analysis. The schematic of methodology employed is shown in Fig. S4 (Supplementary Material).

## 3. Results and discussion

### 3.1. Materials

Nanosized titanium appeared as nanoparticles with a mean volume diameter of 35 nm (Fig. 2a and c). The specific surface area of nano-Ti obtained by the gas sorption technique turned out to be

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