RESEARCH OF COMPOSITE NANOSIZED OXIDES $(TiO_2)_X(SiO_2)_{1-X}$ AND Si-C-O_X SYNTHESIZED USING A NON-EQUILIBRIUM PLASMOCHEMICAL PROCESS

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The results of investigations into the properties of composite nanosized powders of $(TiO_2)_x(SiO_2)_{1-x}$ and Si-C-O_x are given. The powders are synthesized using a non-equilibrium plasmochemical process initiated by a pulsed electron beam. The initial gas mixture consists of oxygen, hydrogen, and a mixture of halides ($TiCl_4$+ $SiCl_4$ or $SiCl_4$+CCl_4) with the total pressure of 400 – 700 Torr. The average grain size of the synthesized powder is 29 nm for $(TiO_2)_x(SiO_2)_{1-x}$ and 47 nm for Si-C-O_x. The paper presents the results of TEM examination, X-ray diffraction and X-ray fluorescence analyses, and IR spectrometry. It is found that the composite nanosized $(TiO_2)_x(SiO_2)_{1-x}$ powder has a crystal structure, while Si-C-O_x is amorphous. It is demonstrated that the process of the synthesis is volumetric. The energy consumed by the electrophysical setup to synthesize the powder is 0.1–0.15 (kW·h)/kg and the output rate is 1–1.1 kg/h calculated per final reaction product. It is shown that it is the non-equilibrium character of the process that makes it possible to lower the temperature threshold for the crystalline structure to develop in the product particles.

Introduction

The use of non-equilibrium plasmochemical processes is of great promise for the synthesis of nanosized oxides. It is their non-equilibrium character that provides a possibility to considerably reduce the energy consumption for the reaction and change its conditions. A non-equilibrium process initiated by a pulsed electron beam is used to synthesize nanosized silicon dioxide [1] and titanium dioxide [2]. The energy of the electrophysical installation consumed to convert silicon tetrachloride ($SiCl_4$) is as low as 0.02 eV/molecule. The aim of this work is to study nanosized $(TiO_2)_x(SiO_2)_{1-x}$ and Si-C-O_x powders synthesized in a non-equilibrium plasma chemical process under a pulsed electron beam.

For the synthesis of a composite $(TiO_2)_x(SiO_2)_{1-x}$ material, use is largely made of the sol-gel method. The resulting amorphous material is further subjected to thermal treatment at the temperature above 500 °C to remove the hydroxyl group and the precursor material left. The crystal phase of the composite $(TiO_2)_x(SiO_2)_{1-x}$ of the rutile type has been formed in minor quantities at the pyrolysis temperature 1100 ˚C only [3-4].

Fig. 1 shows the TEM image of the powder and the bar chart of the grain-size distribution. Note that the mean size of the composite powder particles is smaller compared to that of pure nanosized titanium dioxide synthesized under similar experimental conditions [4]. This might be attributed to changes in the conditions of coagulation of the particles formed upon addition of a new material.

The chemical composition of the synthesized composite powder has been determined in an Oxford ED2000 X-ray fluorescence spectrometer. Taking into account the content of oxygen in the synthesized composite powder, the impurity concentration is less than 0.4 %. Figure 2 shows the X-ray diffraction patterns from two specimens of the synthesized oxides (rad. Co, λ =1.7901 A), and the table presents the data on the proportion of rutile and anatase phases of $(TiO_2)_x(SiO_2)_{1-x}$ for different specimens.

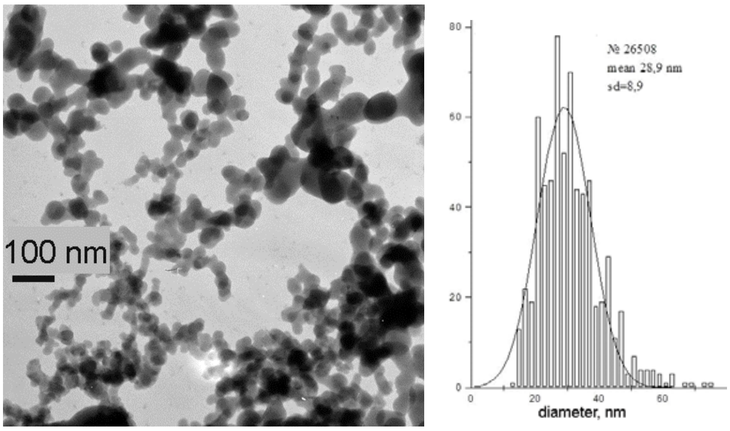

Fig. 1. TEM image and the bar chart of the grain-size distribution from $(TiO_2)_x(SiO_2)_{1-x}$ powder. The mean size is 29 nm. The initial mixture in mmol: $H_2 + O_2 + SiCl_4 + TiCl_4$ (50 : 25 : 17 : 10)

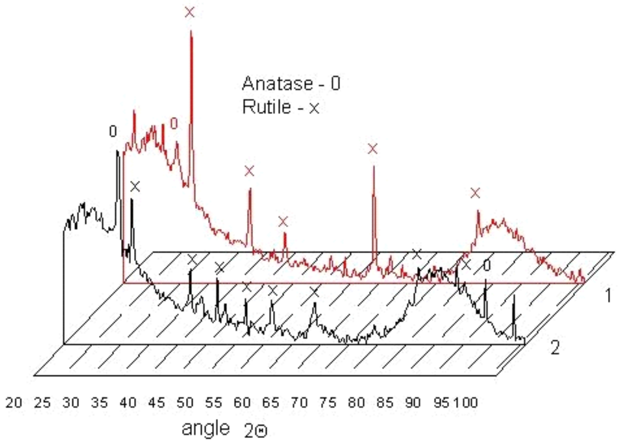

Fig. 2. The X-ray diffraction pattern from the nanosized $(TiO_2)_x(SiO_2)_{1-x}$ powder (curves 1 and 2 correspond to the table data)

Table 1.

Specimen	Synthesis regime	Rutile	Anatase
1	46 mmol H_2+ 23 mmol O_2 +25 mmol $SiCl_4$+ 9 mmol $TiCl_4$	85%	15%
2	46 mmol H_2+ 23 mmol O_2 +25 mmol $SiCl_4$+ 18 mmol $TiCl_4$	47%	53%

The experimental research carried out in this work has demonstrated that a plasmochemical process initiated by a pulsed electron beam is an effective way to synthesize nanosized composite oxides from a gas-phase mixture of oxygen, hydrogen, and a mixture of halides. The resulting nanooxides exhibit homogeneous composition and their particles are spherical in shape with facetting and without voids. A change in the chemical composition of the initial mixture allows one to vary a crystalline structure, a shape and a size of the synthesized particles. The measurements made have shown that the gas-phase mixture temperature in the course of synthesis is maintained not higher than 600 ºC, and the duration of the process is less than 0.1 s.

An outstanding feature of the proposed method is a considerable reduction in temperature for the synthesis of particles with crystalline structure (rutile and anatase), which is due to the non-equilibrium character of the process.

References

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