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Optical properties and radiation stability of submicro- and nanopowders titanium dioxide measured *in situ*

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HIGHLIGHTS

- Reflectance of the submicro- and nanopowders TiO_2 powders measured *in situ.*
- Powders irradiated by 30 keV electron with fluence of 0.5, 1, 2×10^{16} cm^{-2}.
- High radiation stability has TiO_2 particle with 80–160 nm size.
- The maximum absorption bands cause by $Ti_i^{\bullet\bullet\bullet\bullet}$, $V_{Ti}^{''''}$, $V_{Ti}^{'''}$, V_O^{X} defects.
- Nanopowders with 60 nm size have high recovery of reflectance in the residual vacuum.

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ABSTRACT

This study carried out an *in situ* and external investigation on the reflective spectra of micro- and nanopowders titanium dioxide before and after irradiation by 30 keV electrons. The particle sizes range from 60–240 nm. It was established that the decrease in the particle size leads to an increase in intrinsic defects. The particles with intrinsic defects are then transformed into absorption centers during irradiation as a result of optical degradation of TiO_2 powders. High radiation stability has particle sizes range from 80–160 nm.

1. Introduction

Metal oxide powders are widely used in various fields of technology and industry. Titanium dioxide has a special place among them, because of its properties and range of applications. It is one of the major photo-catalysts and pigments for common paints. In spacecrafts it is used as the thermal control coating pigments (Tribble et al., 1996; Zeng et al., 2003; Zhang and Chen, 2004). In visible light-emitting diodes, TiO_2 performs the same function as in the solar-cells, namely that of reflecting light beams from crystals, which are emitted by phosphors (Lee and Yoo, 2011).

In the case of such application the primary role belongs to surface condition. Therefore, the study of processes occurring in the surface and subsurface layers under external influences on powders provides scientific and practical importance.

These influencing factors include different types of radiation. Solar spectrum quanta, absorbed in the surface layers of powders, interact with photo-catalysts and reflecting layer pigments, common paints and thermal control coatings.

It is important to note that the electrons with 10-100 keV energies and protons of solar wind plasma has the highest flux intensity in the spectra of charged particles in outer space (Richard and Armstrong, 1979; Mikhailov et al., 2014a, 2014b). Their range was from nano- to micrometers, and they create a variety of defects on the surface and in volume of surface layers. Therefore, test simulation with such energy values are important for understanding the defect mechanisms formation for space materials, as opposed to the nuclear industry which are characterized by the MeV energy particles.

One of an effective way to increase radiation stability of metal oxides and other materials is the modification by nanoparticles,

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which then become centers of defects relaxation. This reduces the concentration of defects and improves radiation stability of materials (Mikhailov et al., 2011; Li et al., 2013; Mikhailov and Sokolovskii, 2006). Size of micro- and nanoparticles is comparable with the depth-path of charged particles.

Therefore, the study of reflectance spectra and their changes under the radiation of TiO_2 powders with other sizes grain has scientific and practical interest. The absorption bands of the donor-type defects for TiO_2 are near the following values of the energy quanta (in eV) (Janusz, 2008; He et al., 2007; Chena et al., 2001; Seebauer and Kratzer, 2006; Isao et al., 2000; Kuznetsov and Serpone, 2009): the interstitial ions titanium $Ti_i^{\bullet}$ −3.08, $Ti_i^{\bullet\bullet}$ −2.48, $Ti_i^{\bullet\bullet\bullet}$ −2.22 or 1.47–1.56, and $Ti_i^{\bullet\bullet\bullet\bullet}$ −1.71, and the oxygen vacancies are $V_O^{\bullet}$ −2.53 or 1.78, $V_O^{\bullet\bullet}$ −2.11 or 1.18 and V_O^{X}−0.877. The acceptor defects include the following: interstitial oxygen $O_i^{\prime}$−2.69, $O_i^{\prime\prime}$−1.95 and titanium vacancies $V_{Ti}^{\prime\prime\prime\prime}$−1.71 or 1.44, $V_{Ti}^{\prime\prime\prime}$−1.15 or 0.82.

In this paper presents the results of investigations of the optical properties and radiation stability of TiO_2 powder with particle sizes in the nano and submicro ranges. The measurements were performed in vacuum (5×10^{-7} Torr) *in situ* under 30 keV electrons exposure, which is characteristic of the electrons spectra in orbits. Such researches are important for the thermal control coatings of spacecraft.

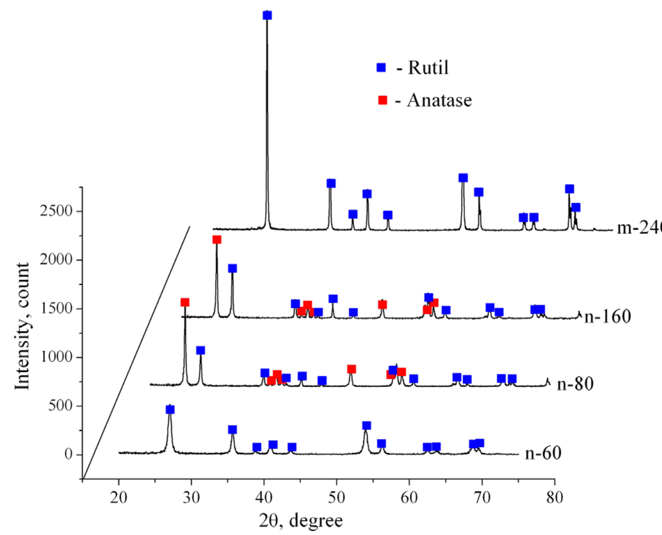

Fig. 2. XRD patterns of TiO_2 submicro- and nanopowders.

2. Materials and methods

The objects of this research are submicron size industrial production TiO_2 powder obtained from “Kronus” company with an average size of particles 240 nm (m-240) and nanopowders obtained from “Plazmoterm” company with an average size particle of 60 (n-60), 80 (n-80) and 180 (n-160) nm (Fig. 1). The specific surface area of powder m-240, n-160, n-80, n-60 is at 8, 13, 16 and 28 m^2/g respectively.

Submicron powder has the lattice of rutile, nanopowders have both the lattice of anatase and rutile (Fig. 2). The ratio of these phases has changed within changing particle size. For particle size 160, 80 and 60 nm concentration of rutile changing as 50.0, 33.9 and 98.7 wt%, the anatase concentration was at 49.8, 66.1 and 1.3 wt%.

Samples were prepared by 1 MPa pressure of the powders in metal cups 28 mm diameter, 2 mm depth. Samples have been fixed on the table in space environment simulator “SPECTR” (Kositsyn et al., 1985). In the chamber was set high vacuum (5×10^{-7} Torr). Diffuse reflection spectra measured within the range from 300–2000 nm by integrated sphere. Then the samples were irradiated by electrons with energy 30 keV with fluence of 0.5, 1, 2×10^{16} cm^{-2}. The electron flux during irradiation was 4×10^{11} $cm^{-2}s^{-1}$. Irregularity of the electron beam on the area sample did not exceed 5%. It was determined by the method of the slit diaphragm (Kositsyn et al., 1985). The choice of 30 keV electron energy is due to the fact that electrons with energies of 10–100 keV have the greatest flux in orbits, such as geosynchronous equatorial orbit. The main components of the residual gases at this pressure were H_2, N_2, CO_2, and Ar. The partial pressure of oxygen was approximately 10^{-10} Torr. After each radiation exposure the spectra were measure in a vacuum (*in situ*). The samples were fixed on the specimen stage which was thermostated at 300 K. Therefore, the temperature of all samples was the same as during measurement of reflectance spectra, and irradiation. Thereafter the powders were displacement in the residual vacuum 10^{-1} Torr for 100 h and afterwards their reflectance spectra were measured.

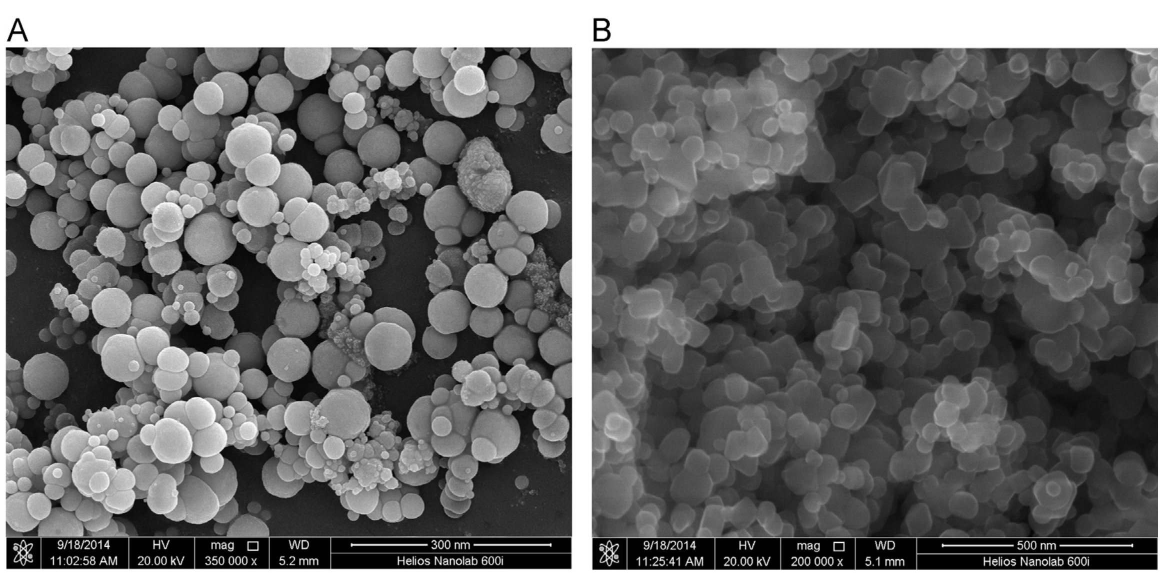

Fig. 1. SEM graphs of n-160 (A) and n-80 (B) nanopowders.