RADIATION STABILITY OF COATINGS BASED ON TiO₂, ZnO AND SiO₂ NANOSTRUCTURED PIGMENTS TO PROTON EXPOSURE

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ABSTRACT

The effect of protons (E = 100 keV, F = 5 x 10^{15} cm⁻²) exposure on the diffuse reflectance spectra of the coatings based on the TiO₂, ZnO and SiO₂ microsphere pigments in wavelength range from 250 to 2500 nm have been investigated. Evaluating the changes of the solar absorptance it was found that the radiation stability of the SiO₂ sphere particles coatings is higher than the radiation stability of TiO₂ and ZnO hollow particles coatings as well as the standard coatings based on this micropowders. The low radiation stability of the SiO₂ sphere particles is due to low radiation losses, low concentration of radiation-induced defects cause by presence of amorphous phase.

1 INTRODUCTION

The impact of the space environment on spacecraft leads to changes in properties and performance of the external materials, especially to increase in solar absorptance of thermal control coatings (TCC). The impact of space radiation is affected to spacecraft passing through all types of orbits from LEO to GSO. To a great extent it concerns white TCC of the class "solar reflectors", which include ceramic and enamel coating based on white pigments, polymer, and inorganic bonding agents [1]. The powders of SiO₂, TiO₂, ZnO had the widest application among the pigments for coatings of this class due to their high stability to impact of charged particles and solar ultraviolet radiation. However, a number of defects and absorption centers are formed in these pigments during a long-term spacecraft flight, which is enough to decrease the spectral reflectance in the ultraviolet (UV), visible and near-infrared (NIR) regions of the spectrum, and increase the solar absorptance (αₕ) [2]. Therefore, the development of ways to increase radiation stability of coatings based on titanium dioxide is an urgent problem.

One innovating technique to improve the photo- and radiation-stability of coatings is to use microspheres as pigments, which are hollow particles with a high specific surface area. In such structures, radiation defects in bulk are less, as well as the surface defects being recombined on the thinner layer of the microspheres.

It is known that in conventional coatings based on polycrystalline oxides as pigments currently in use (Fig.1.(a)), the primary radiation defects produced from proton and electron exposure with energy below 300 keV are formed in layers approximately 5 μm, but secondary and thermalized defects may extend into deeper layers of the coating [3]. The color centers formed in polycrystals by radiation primarily impact on the optical properties of the coating, specifically on the reflectance and absorptance that are determined by a thickness of 80 μm.

One prospective new technology to improve the photo- and radiation-stability of coatings is to use microspheres as pigments, which are hollow particles with a high specific surface area. In such structures, radiation defects in bulk are less, as well as the surface defects being recombined on the thinner layer of the microspheres (Fig.1.(b)). The major portion of ions in ionizing radiation results in the creation of the defects in the depth of coatings (over 100 μm), due to the low ionization losses in the hollow particles. Thus, the defects formed in the depth of the material have the least effect on the optical properties of the coating. Also
nanostructured materials such as microspheres have low weight and low thermal conductivity compared with the pigment-polycrystalline that decreases the overall weight of a spacecraft. This paper is devoted to the analysis of the reflective spectra of SiO$_2$, TiO$_2$, ZnO hollow particles and coatings based on them in the region of 200-2500 nm before and after irradiation by protons, and comparison of the obtained regularities with the data of coatings based on micropowders.

**2 EXPERIMENTAL**

The TiO$_2$, ZnO and SiO$_2$ micropowders with 99.8 % purity were purchased from Aladdin Chemistry Co. The synthesis of the TiO$_2$ and ZnO microsphere was carried out by the hydrothermal method [5], but SiO$_2$ by the formation of silica shells and dissolution of the polystyrene core particles. Synthesis of hollow TiO$_2$ particles was carried out as in [6]: 17.5 mmol Zn(CH$_3$COO)$_2$·2H$_2$O dissolved in 1 l of water, then in the resulting solution was added tetraethylammonium hydroxide ((C$_2$H$_5$)$_4$N$^+$OH$^-$) and stirred on a magnetic stirrer for 30 minutes. The resulting solution was poured into an autoclave with Teflon cup which was heated at air. After natural cooling the autoclave was opened, the powder precipitate itself, which was washed several times with ethanol and ammonia water, (OC$_3$H$_7$OH) on solid substrates in the form of polystyrene beads in a solution of alcohol and ammonia water, followed by heat treatment at 600 °C for 3 hours.

Hollow SiO$_2$ particles were obtained by depositing Si (OC$_3$H$_7$)$_4$ on solid substrates in the form of polystyrene beads in a solution of alcohol and ammonia water, followed by heat treatment at 600 °C for 3 hours.

Hollow TiO$_2$ particles were obtained by hydrothermal method [7]: 2.5 mmol Zn(CH$_3$COO)$_2$·2H$_2$O was dissolved in 1 mol deionized water, after which 7.5 mmol NH$_4$HCO$_3$ was added. The solution was poured into a Teflon-lined autoclave, which was filled to 80 %. The sealed autoclave was maintained at 180 °C during 15 hours. After natural cooling the autoclave was opened, the white product were collected and sequentially washed several times by deionized water and ethanol. The centrifugation was not performed, the powder precipitate itself, which was dried at 80 °C at air.

Hollow SiO$_2$ particles were obtained by mixing the powders with 50 % of volume and binder with 50 % of volume. The binder was a modified silicone varnish (methyl and methoxy group containing polysiloxane), with small additives of epoxy resin and some amount of hardener and stabilizers. The paint was coated with thickness 150-200 µm on the aluminum substrate 17 mm in diameter. The coating was sprayed by the airless method, which was obtained by dispersing the flow of the paint material.

Samples were tested using the Space Environment Simulator. The samples were irradiated by protons with energy of 100 keV fluence $5 \times 10^{15} \text{ cm}^{-2}$ with the flux $5 \times 10^{11} \text{ cm}^{-2}\text{s}^{-1}$ in vacuum $2.5 \times 10^{-4} \text{ Pa}$, while the initial vacuum was $5 \times 10^{-3} \text{ Pa}$. Irregularity of the proton beam on the area sample did not exceed 5 %. During irradiation samples were maintained at 300 ± 5 K temperature.

The surface morphology of the hollow particles was analyzed by the scanning electron microscope (SEM) Helios NanoLab 600i and ZEISS EVO18. The specific surface area of the powder is determined by Brunauer-Emmet-Teller (BET) method with physical adsorption of nitrogen using AutoSorb 6iSA technique. The X-ray diffraction (XRD) analysis was carried out on a diffractometer Philips X’Pert PRO MRD (V = 40 kV, I = 40 mA, CuKα = 1,5405). The reflective spectra of the samples were measured using a Perkin Elmer Lambda 950 spectrophotometer with a scanning rate of 5 nm/s and a wavelength range from 250 to 2500 nm. The value of solar absorbance of the samples was calculated in accordance with ASTM (E490 and E903-00a-96).

**3 RESULTS**

From the micrographs obtained by the scanning electron microscope (Fig. 2) showed that during the reaction TiO$_2$, SiO$_2$, ZnO particles with a spherical shape 1-10 µm in average size are formed. The yield of hollow particles is about 90 %, other particles are bonded together or are the fragments of the spheres. The specific surface area (SSA) of the synthesized particles measured by BET are presented in the table 1, measurements were carried out for two powders synthesized in different experimental series. The highest SSA value among microspheres is typical for TiO$_2$, but a high SSA value for the microcrystal is for ZnO.
In the near IR region it has been established that the microcrystals of SiO₂, TiO₂, and hollow particles are in the range from 400 to 1200 nm, in the near IR region it decreases to 35%. In this region, the absorption bands of the binder, some of them coincide with absorption bands of SiO₂, TiO₂, and hollow particles. In the UV region, a "dip" is recorded for the hollow particles of TiO₂, whereas for microparticles there is no absorption in this region. Reflectance values for hollow particles in the region above 400 nm are 5% greater than in micropowders. In the UV region, a "dip" is recorded for the hollow particles - a decrease in the values of ρ to 40%.

It follows from the XRD patterns that a diffuse peak is observed in the region 21° for micro- and hollow powders of silicon dioxide, which indicates the amorphous phase of SiO₂ (Fig. 4b). Peaks indicating the presence of crystalline phases of silicon dioxide are absent.

It follows from the diffuse reflection spectra (Fig.5) that the spectral reflectance in the UV and visible regions reaches 90% for micro- and hollow powders of ZnO and TiO₂. The reflectivity of the micropowder is higher than that of hollow powders in the wavelength region from the edge of the main absorption to the near IR region. The smaller value of the spectral reflectance of hollow powders is due to the high concentration of intrinsic defects in the crystal lattice of nanostructured particles relative to the microparticles. At the same time, there is a competing process of increasing the reflectance by nanoparticles, associated with the scattering of light by small particles. In the near-IR region, the reflection coefficient of hollow powders is significantly reduced in comparison with micropowders. The difference in ρ values reaches 15-40%, which is determined by the high concentration of free charge carriers and chemisorbed gases absorbing in this spectral region [9]. The effect of decreasing the reflectance in the near-IR region is typical for hollow SiO₂ particles, whereas for microparticles there is no absorption in this region. Reflectance values for hollow particles in the region above 400 nm are 5% greater than in micropowders. In the UV region, a "dip" is recorded for the hollow particles - a decrease in the values of ρ to 40%.

X-ray diffraction analysis showed (Fig. 2b) that the synthesized hollow TiO₂ particles have peaks related to the anatase structure (P41/amd), there are no amorphous phases. The parameters of the unit cell for hollow particle are: a = 3.873 ± 0.003 Å, c = 10.50 ± 0.008 Å. For microparticles it is equal: a = 3.799 ± 0.002 Å, c = 9.756 ± 0.003 Å. Such changes of constant lattice are associated with various tensile stresses caused by packing defects and leading to inelastic deformation of the grating. For hollow particles such distortions occur along the c axis, for nanoparticles tensile stresses act along the a axis.

Changes in the lattice constants occur also in nano- and hollow particles of zinc oxide (P63mc). The structural type of these powders is wurtzite. The constants of the crystal lattice of the microparticles were: a = 3.249 ± 0.003 Å, c = 5.205 ± 0.004 Å. For nanoparticles, it has been established that the parameters a and c increase to 3.2549 ± 0.002 Å and 5.2104 ± 0.003 Å, respectively. Values of lattice parameters a and c for hollow particles are in the range between the values for micro- and nanoparticles.
with the absorption bands of micropowders. For coatings based on SiO₂ is typical decrease of the reflectance in the region from 400 to 1200 nm to 60%. Such low value of reflectance was not typical for powders for which a reflectance reached 95% in the UV region.

![Image](57x537 to 283x702)

**Fig.6** Diffuse reflectance spectra of coating based on hollow and microparticles of ZnO, TiO₂, SiO₂.

From the spectra of induced absorption after proton irradiation (Δρ_{E} = ρ_{ED} - ρ_{EF}, where ρ_{ED} and ρ_{EF} are the spectra of diffuse reflection before and after irradiation, respectively) with an energy of 100 keV, fluence 5×10^{15} cm⁻² (Fig. 7) powders of micro- and hollow particles it follows that the effect of ionizing radiation creates color centers whose bands form a continuous absorption spectrum in the UV and visible regions. ZnO powders are characterized by absorption bands with a high intensity in the range from 2 to 3.2 eV, in the near-IR region the intensity of the bands is insignificant. The high intensity bands have hollow particles of zinc oxide, the smallest – microparticles. The integral absorption band for hollow particles is shifted to the red region, the intensity of which closely coincides with the band for the microparticles.

After irradiation of TiO₂ powders, protons in the induced absorption spectra show absorption bands in the visible and near-IR regions. In the spectrum of micropowders, the intensity of the absorption bands in the short-wave region is larger than the intensity of the bands in the visible and near-IR regions. A distinctive feature of these spectra is that in the absorption spectra of powders from hollow particles there is practically no absorption in the near-IR region, while in the micropowder spectra it is not only recorded, but in absolute value, close to absorption in the UV region. In the spectra of induced absorption of silicon dioxide, well-separated absorption bands are recorded in the short-wavelength region. The lowest intensity of the bands is characteristic for hollow particles, the largest for microparticles. The bands intensity of SiO₂ nanoparticles is higher in comparison with the intensity of nanopowders ZnO and TiO₂.

![Image](Image 312x604 to 539x771)

**Fig.7** Change in spectral reflectance of hollow and microparticles of ZnO, TiO₂, SiO₂ after 100 keV proton irradiation with fluence 5×10^{15} cm⁻²

From the analysis of the spectra Δρ_{E} of proton-irradiated zinc oxide powders with micron-sized grains, taking into account the known energy of the absorption bands of intrinsic defects, capable of absorbing in these ranges [10-15], it follows that the main contribution to the absorption is made by interstitial zinc ions Zn⁺, oxygen vacancies V₀⁺⁺, zinc vacancies V₉⁺ and V₉⁺⁺. Nanopowders irradiated by protons have a similar spectrum of Δρ_{E} with micropowders, but the intensity of the bands in their spectra is higher. For both micro- and nanostructured particles, the absorption bands in the energy range from 1 to 2 eV have a low intensity. These bands are due to the interstitial oxygen O₁⁺ and O₁⁺⁺ and vacancies of oxygen V₀⁺⁺.

For titanium dioxide, the absorption in the UV region is determined by the defects of the cation sublattice, in the near-IR region by the defects of the anion sublattice [16-21]. After irradiation of the hollow particles, vacancies of the cation sublattice are formed to a lesser extent, which include vacancies V₉⁺⁺⁺⁺ and V₉⁺⁺⁺⁺. At room temperature, they correspond to absorption bands at 1.15 and 1.44 eV. This conclusion is typical not only for hollow particles of titanium dioxide powders, it is also valid for powders of this compound of micron sizes modified by nanoparticles of other compounds, as well as enriched in oxygen by various methods: treatment with tetro- and peroxoborates and peroxides, treatment with ultraviolet in oxygen and in the atmosphere [22]. In all these cases, a significantly lower intensity of the absorption bands by defects in the cation sublattice is recorded in comparison with the defect bands of the anion sublattice.

The energy position of the bands of radiation-induced absorption in the spectra of micro- and hollow powders of SiO₂ is the same or very close. In the high-energy region of the spectrum, a band is recorded at 5.96-6.02 due to the surface centers of E', [23-27] and the band at 5.46-5.48, determined either by vacancies in oxygen (E₀') or by oxygen vacancies, which captured hydrogen
atoms (E'). In the low-energy region of the spectra, the absorption bands at 4.45-4.5 are referred to the surface centers of E'.

In the absorption spectra of the coatings (Fig. 7), samples of coatings from micropowders TiO₂ have the highest absorption, the peak of which lies in the visible region of 3.08 eV, which coincides with the value of the pigment. For hollow particles, the position of the peak absorption is close to 2.7 eV. The high absorption in coatings based on TiO₂ microspheres has a value in the peak near 55%. It follows from this that the degradation of optical properties of coatings from TiO₂ microspheres is smaller in comparison with coatings from micropowders TiO₂. A similar pattern is observed for coatings based on hollow and microparticles ZnO, a high intensity of the integral band for coatings based on hollow powders, which values are 63%. At the same time, we observed a different situation in describing the degradation of optical properties for which zinc oxide powders irradiated by protons, where the concentration of radiation defects causing the integral absorption band was higher for hollow ZnO particles. Degradation of coatings based on hollow SiO₂ particles under the action of 100 keV protons also occurs less intensively than coatings based on SiO₂ microparticles. Moreover, the intensity of the integral band has the smallest values (42%) of the investigated coatings based on ZnO and TiO₂. It should be noted that this band is somewhat tightened in the UV region of the spectrum and width at half-height low than the integral band of coatings based on ZnO.

From the physical point of view, it is also convenient to estimate the optical properties from the solar absorptance since the absorption bands of the defects in ZnO, TiO₂ and SiO₂ powders are located in different regions of the spectrum. Whereas the radiation stability is conveniently estimated from the change in the solar absorptance (Δαs).

After calculating the solar absorptance it follows (Table 2) that the smallest value of αs has microcrystal-TiO₂ coatings. Whereas microspheres based coating shows high optical properties for ZnO. Exposure of the proton irradiation leads to degradation of coatings. It is established that the use of hollow particles leads to an increase in the radiation stability of coatings for all types of particles. The smallest degradation in coatings based on SiO₂ microspheres, but the initial optical properties are not so high. The best combination of the initial optical properties and their radiation stability to the impact of accelerated protons is typically for coatings based on ZnO microspheres. Thus, the efficiency of the SiO₂, TiO₂ and ZnO microspheres particle pigment compare with microcrystal particle pigment are 8 %, 32 % and 36 %, respectively.

<table>
<thead>
<tr>
<th>Coating</th>
<th>αs</th>
<th>Δαs</th>
</tr>
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<tbody>
<tr>
<td>microcrystal-TiO₂</td>
<td>0.17±0.012</td>
<td>0.268±0.023</td>
</tr>
<tr>
<td>microsphere-TiO₂</td>
<td>0.21±0.017</td>
<td>0.203±0.031</td>
</tr>
<tr>
<td>microcrystal-ZnO</td>
<td>0.18±0.011</td>
<td>0.241±0.026</td>
</tr>
<tr>
<td>microsphere-ZnO</td>
<td>0.20±0.011</td>
<td>0.177±0.024</td>
</tr>
<tr>
<td>microcrystal-SiO₂</td>
<td>0.27±0.025</td>
<td>0.132±0.052</td>
</tr>
<tr>
<td>microsphere-SiO₂</td>
<td>0.325±0.032</td>
<td>0.121±0.062</td>
</tr>
</tbody>
</table>

4 DISCUSSION

Defect formation under proton irradiation of oxide powders is caused by radiation damage, which is determined by at least two processes. The first is the ionization mechanism that is characteristic of the surface layer, when a proton with high energy strikes an interatomic bond, destroys it, captures an electron and forms two ionized atoms:

MeMe⁺X + O0⁻X + (H⁺)* → (MeMe⁺X)* + (O0⁻X)* + H⁺,

where MeMe⁺, O0⁻ – atoms of cations and oxygen at lattice sites; (H⁺)*, H⁺ – accelerated and thermolysed proton.

On the surface, random processes of knocking out weakly bound oxygen with the formation of anion vacancies are also possible. In this case, the proton also captures the electron. The knocked out oxygen produces secondary atomic collisions. The second process of primary radiation damage, along with the first one, occurs in the volume of the polycrystal. It is carried out mainly by knocking out atoms from the nodes with the formation of vacancies by the following reactions:

MeMe⁺X + O0⁻X + (H⁺)* → VMe⁻⁻ + MeMe⁺X⁺ + O0⁻X + H⁻ →

VMe⁻⁻ + MeMe⁻⁻ + O0⁻X + H⁻

VMe⁻⁻ + MeMe⁻⁻ ↔ VMe⁻⁻ + MeMe⁺X⁺

MeMe⁺X + O0⁻X + (H⁺)* → MeMe⁺X⁺ + O0⁻X + (H⁻) + H⁺ →

MeMe⁺X + O0⁻X + (H⁻) + H⁺ → MeMe⁺X⁺ + O0⁻X + H⁻ →

Table 2. The values of αs before irradiation and Δαs after 100 keV proton irradiation of coatings based on the TiO₂, ZnO and SiO₂ microcrystal and microsphere particles.
V3+ + O2→ V5+ + O2.
Thermalized hydrogen and oxygen can diffuse from the lattice to the surface of the polycrystal, followed by desorption. The defects remaining after this stage are in equilibrium and can be kept for a long time. These defects will determine the optical properties of the irradiated powder. Thermalized protons can interact with zinc vacancies or interstitial oxygen and form stable defects (V_{Zn}-H) [28].

The products of the destruction of silicone varnish are cyclic oligomers - from the trimer to the heptadecamer. The common mechanism of their formation assumes the emergence of cyclic intermediate structures with the participation of the terminal group, in which the coordinated rupture and bonding occurs [29, 30]:

The increased radiation stability to the action of protons of hollow particles in comparison with microparticles is probably due to the fact that in these particles the probability of radiation defects formation in the volume of spherical particles is small because of the absence of material inside the hollow particle. Such structures also have small ionization losses and a high ability to relax radiation defects in a thin layer of the sphere. The high radiation stability of hollow SiO2 particles can be attributed to the presence of an amorphous structure, where the intrinsic and radiation defects can be reflected in such an unordered structure and restored more quickly.

Improving the radiation stability of coatings based on hollow particles can be due to the formation of metal-organic complexes between the polymers of silicone varnish and inorganic compounds of oxide powders upon irradiation. Under such conditions, the polymer radicals induced by ionizing radiation crosslinked on the developed surface of the hollow particles.

CONCLUSION
In summary, the initial a8 of the coatings based on micropowders is higher than that for the microsphere based coatings. It is found that the radiation stability under proton exposure (100 keV, 5x10^{15} cm^{-2}) of the micropowder based coatings is higher than for the micropowders based coatings. This effect associated with the relaxation defects on high specific surface area of the hollow particles and the low ionization losses therein. Evaluation of other parameters for use such pigments in thermal control coatings will be continued.

REFERENCES
15. Erhart P., Albe K., Klein A., First-principles study of intrinsic point defects in ZnO: role of band


