Effect of particle size on the diffuse reflection coefficient of titanium dioxide powder

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Abstract. In the present work a model of light scattering is shown which explains the result about effect of particle size on the diffuse reflection coefficient of initial titanium dioxide powders. The diffuse reflection coefficient depending on particle size for TiO_2 pigment varies on the curve with maximum. The experimental results and the model can be used for technology development of manufacturing pigment for light-reflecting temperature-control coatings of spacecraft

1. Introduction

During use device uncovered parts are exposed natural background and electromagnetic radiation, which penetrate to material surface layer. The accumulation of defects induced by radiation leads to microscopic changes related to the rupture of the individual valence bonds. These ruptures contribute to the appearance of luminescence centers. Moreover, this contributes to phase transitions and chemical reactions that lead to a change in the atomic structure of the crystal lattice and it properties. These changes are expressed in the ageing or degradation of the materials and coatings.

The main problem of maintaining the stability of the technical devices in radiation conditions is to develop composite materials and coatings that provide the desired level of their initial properties, a sufficiently high degree of protection in case of accidental drift of environmental parameters and the low degradation rate of the desired properties.

In crystals always there is some concentration of equilibrium pre-irradiation defects. As the rule, surface defects concentration increased during milling. This leads to the effect of particle size on irradiation stability. The effect of grain size on the irradiation stability of the materials is investigated in several studies [1-4] and the effect of particle size on the initial properties is shown in papers [5-8].

Titanium dioxide powders-pigments are applied for manufacturing of enamels, white paints and a reflecting temperature-control coatings (RTC) of spacecraft.

In this paper are given explanations about the results of the effect of particle size (r) on the diffuse reflection coefficient (ρ) initial powders using the developed model of light scattering.

2. Experimental techniques

Conducting experiments in real conditions using the spacecraft are connected with the serious technical and scientific challenges. That is why, in the laboratory for the study of irradiation effects in aerospace materials at Tomsk Polytechnic University to test RTC developed and manufactured special settings that simulate of space environment: vacuum, temperature, flow of charged particles (electrons and protons) and electromagnetic radiation, plasma of ionosphere, plasma “Sunny the wind”.

The reflectivity of powders were measured by an absolute method of globular photometer using the "Spectrum" [9] which comprised of a source of electromagnetic radiation imitating solar spectrum in the wavelength range of 0.2 to 2.2 microns; the sources of electrons and protons imitating radiation belts of the Earth also the gas puffing system and control system their partial pressure. The investigated samples are clamped by fixed block to surface copper object stage. There are five clamps which allow to fasten 20 samples having diameter 15 mm. Object stage has a possibility to rotate around axis from magnetic drive this allows to investigate the samples by turn without breaking a vacuum. For control and maintain temperature of samples in range 80-470 K applied a clamping table-thermostat constitute copper ring with a channel for a liquid heat-transfer and electric heater. The temperature is measured by copper-constantan thermocouples caulk in substrate samples.

Absolute method of registration diffuse reflection spectra consist in measurement the illumination produced on a certain portion of the inner surface of the integrating sphere at two different positions of the light beam.

Powder factions were obtained by the sedimentation method based on Stokes' law [10]. The size of the accumulated particles is calculated by the formula from Stokes' law:

$$r = \sqrt{\frac{18 \cdot \eta \cdot U}{(d_2 - d_1) \cdot g}}$$

where d_2 – the density of material particles, d_1 – the density of dispersion liquid, g – free fall acceleration, η – the liquid’s viscosity, U – the deposition rate of particles in a viscous medium.

The powders TiO_2 (collected sample + water) were applied on an aluminum substrate whereupon a suspension was dried during 24 hours at the room temperature. Samples were fixed on the object stage of setting "Spectrum", atmosphere in vacuum chamber was to 10^{-5} Pa, the initial diffuse reflection spectra were recorded in the range 360-2100 nm at 300 K and samples were irradiated by electron flux from $7 \cdot 10^{15}$ up to $4 \cdot 10^{16}$ cm^{-2} with 30 keV energy and intensity $1 \cdot 10^{13}$ cm^{-2}s^{-1}. After each irradiation step we recorded the diffuse reflection spectra of irradiated samples in vacuum. Diffuse reflection spectra ($\Delta\rho_\lambda$) were calculated by subtracting the spectra ρ_λ before and after irradiation and equated to the induced absorption spectra.

3. Result and discussion

We have previously found [11] that the dependence of diffuse reflection in different regions of the spectrum before irradiation (ρ_1), after irradiation by electrons (ρ_2) in the range of the average particle size 1-15 microns TiO_2 powder varies along a curve with a maximum and the dependence $\Delta\rho = \rho_1 - \rho_2$ varies along the curve with the minimum. In the area with the greatest reflection of initial powders observed maximum of irradiation stability. The optimal particle size lies in a range 2-4 microns. Increasing irradiation stability by varying the particle size for TiO_2 powders is over 5%.

Reducing diffuse reflection with increasing particle size explained the technological conditions of prepare samples. The increasing diffuse reflection with increasing particle size is explained by geometric factors considered powder system (scattering model). The rise $\Delta\rho$ with decreasing particle size is explained by defects emerging during formation a new surface. These defects in the initial condition are centers of gas sorption, but in the case when it located under action before-threshold irradiation it becomes potential color center. On the other hand an increase in the specific surface area decreases the concentration of defects, due to their drain on the dislocations to the surface of the crystallite, where occurs dissipation of energy electronic excitations.

Next, we consider the theoretical model of light scattering crystallites spherical form in more detail, which explains the growing part of the diffuse reflection from particle size. This model assumes existence of two light sources: 1) surface source - in a crystallite shape with size r_A; 2) volumetric source - in shape of scattering center with size r_C. For simplicity, let's consider the particles of spherical shape (Figure 1), where there are m scattering centers in volume.

Assume that scattering coefficient has constant value σ_C on the one center, on surface – σ_S. In this case, scattering coefficient of single particle can be written as $\sigma_P = W_S \sigma_S + W_C + \sigma_C$ or in expanded form:

$$\sigma_p = \sigma_S + \frac{r_C^2}{r_A^2} m \sigma_C \qquad (1)$$

where W_S=1, $W_C = \frac{r_C^2}{r_A^2} m$ - the probability of ingress of luminous flux to the surface and the

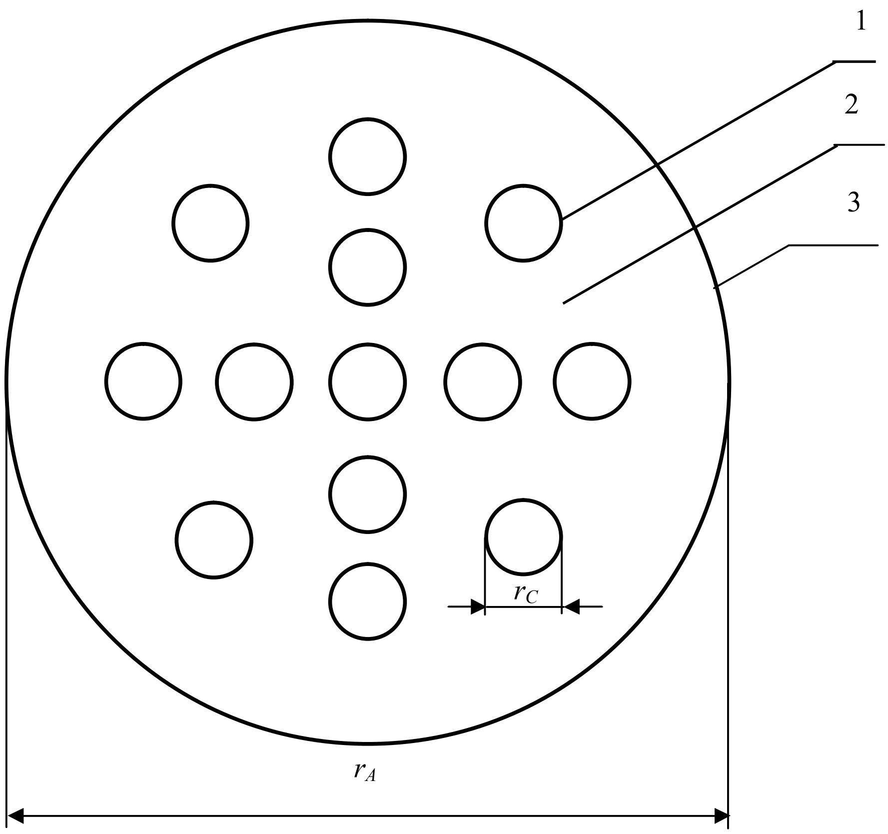

Figure 1. The scattering model: 1 – scattering center; 2 – perfect crystal lattice; 3 – scattering surface of crystallite.

scattering centers respectively; $\frac{r_C^2}{r_A^2}$ – the relative area of the one center.

Assuming that $\sigma_S \approx \frac{\pi \cdot r_A^2}{2}$ and $\sigma_C \approx \frac{\pi \cdot r_C^2}{2}$, the particle scattering coefficient is obtained from (1):

$$\sigma_P = \frac{\pi}{2} r_A^4 + \frac{\pi}{2} \frac{r_C^4}{r_A^2} m = \frac{\pi}{2} (r_A^4 + r_C^4 m)$$

Thus, the more r_A, the more σ_p.

This means, that reflecting surface of crystallite are increased with increasing particle size, and consequently diffuse reflection coefficient are increasing.

4. Conclusions

The diffuse reflection coefficient depending on particle size varies along a curve with a maximum. The highest irradiation stability is observed in an area of the greatest reflection unexposed initial powders. Particles which provide high values of diffuse reflection coefficient in sunny range of spectrum and good the TiO_2 powder stability to the action of electrons have a size in range from 2 to 4 microns. The increasing diffuse reflection with increasing particle size is explained by geometric factors considered powder system. A model of light scattering crystallites spherical shape was offered, which explains this increase.

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