Modified tungsten oxide-based filler for radiation protective polyimide composites

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Abstract. The paper presents the results of studies on surface modification of finely dispersed tungsten (IV) dioxide with polyethylsiloxane from a solution of n-hexane with the aim of its compatibility and the possibility of uniform distribution in the volume of the nonpolar polyimide matrix. The energy dispersive interaction of the press powder of polyimide and highly dispersed modified WO$_2$ in a jet-vortex mill allowed for the activation of their surface, as well as high uniformity of distribution of the filler in the polyimide matrix and excluded the possibility of the formation of agglomerates. It is shown that the use of modified WO$_2$ increases the degree of filling of the polymer composite by 15-20% and the increase in the density of the composite by 16.0%.

1. Introduction
Currently, there are increased requirements for the radiation safety of spacecraft, in particular, for radiation protection materials. The safety of spacecraft is determined not only by protection from external cosmic radiation, but also from the radiation of radioactive sources of used nuclear power plants (NPP). It is necessary to ensure the radiation protection of both the personnel of the spacecraft and the electronic equipment of the basic supporting structures in order to increase their reliability and service life up to 15 years. It must be borne in mind that the ionizing radiation level in the orbit of the International Space Station (ISS) is about 200 times higher than on Earth.

An alternative to the existing radiation protection based on heavy metals and light metal hydrides for space NPP can be considered polymer composite materials [1-3]. However, the use of known polymer composites for radiation protection of spacecraft is limited by a narrow thermal stability interval (from -50 °C to 120 °C), degradation of electrophysical and mechanical characteristics of polymer composites under the influence of vacuum ultraviolet, fast electrons, protons, atomic oxygen and high-energy gamma radiation [4, 5]. In this regard, a new approach is needed to design effective radiation protection for spacecraft (including nuclear power plants) based on polymer composites with enhanced radiation and thermal resistance, capable of ensuring the radiation safety of personnel and uninterrupted operation of the onboard electronic systems with a reduced mass of radiation protection.

For the protection of aerospace electronics devices, the most promising are composites based on polyimides filled with highly dispersed heavy metal oxides. The use of polyimide is due to its high mechanical characteristics, radiation and chemical resistance, as well as a wide operating temperature range (from -250 °C to +350 °C), as well as a very low outgassing effect of high vacuum, which distinguishes it among heterochain thermoplastics and determines long-term use in space conditions [6]. Despite extensive studies of polyimide composites (glass and carbon plastics) and the Kapton-HN
polyimide film from Du Pont (USA) for spacecraft, there are no data on the development of radiation protective polyimide matrices filled with tungsten (IV) oxide.

Due to the hydrophilicity of tungsten dioxide, pre-modifying its surface with low molecular weight oligomers (for example, polyalkylhydrosiloxane) will ensure compatibility and the possibility of uniform distribution of the filler in the volume of the non-polar polyimide matrix.

In this regard, this paper presents the results of studies on the surface modification of tungsten oxide and the effect of modification on the density measurement of a filled polyimide composite.

2. Materials and methods
Fine-dispersed tungsten (IV) dioxide powder was used as a radiation-protective filler, the choice of which is due to its high density of 12.1 g/cm³, thermal stability, non-toxicity and wide technological capabilities.

The fractional composition of solid particles of tungsten oxide was investigated by laser scattering on a «MicroSizer 201» diffraction microanalyzer.

Ultrasonic processing of the powder of tungsten oxide was carried out at a frequency of 22 kHz.

As a modifier, polyethylsiloxane is used in the form of a hydrophobic liquid 136-41 (GOST 108034-76). Modification was carried out from a solution of n-hexane by static mixing of the suspension for 1 hour at a temperature of 20 °C, followed by separation of the precipitate by centrifugation.

Thermoplastic polyimide in the form of press powder (particle size 2-5 microns) was used as the polymer matrix. The composite material was pressed on a PSU-50 hydraulic press at a specific pressure of 200 MPa using a steel mold with constant heating and holding at a temperature of 325 °C to soften the polyimide material, its transition to a viscous-flowing state and polymerization of polyimide.

3. Results and discussion
The simplest modification option is the adsorption of organic polymers on the metal oxide surface [7, 8], and the possibility of fixing the modifier on the filler particles is mainly due to the presence of active hydroxyl groups (–OH) on their surface. An important factor of modification is the uniformity of the formation of a modification shell on the surface of tungsten dioxide of monodisperse spherical particles [9–13].

Preliminary preparation of the powder of tungsten oxide for the purpose of fixing the groups (–OH) was in wet grinding, followed by boiling and sonication with a frequency of 22 kHz.

As a result of abrasion and grinding, there is an increase in the concentration of surface defects of the filler, which is caused by the breakdown of contacts between the crystals with a rupture of covalent bonds. Ultrasonic treatment also allows one to increase the number of defects in the crystalline state, the surface energy of the oxide and create a favorable developed relief [14].

The fractional composition of the powder of tungsten oxide obtained by wet grinding for 6 hours and ultrasonic treatment with an oscillation frequency of 22 kHz for 30 minutes is shown in Figure 1.

After physicomechanical processing, a large proportion of WO₂ particles have a size of 0.5–2.0 μm, which makes it possible to create a composite with a high degree of homogeneity, while the polyfractional composition makes it possible to achieve a high degree of packing.

Boiling, like previous processing methods, contributes to the forced hydroxylation of the surface of tungsten (IV) oxide powder according to the scheme:

\[
\text{WO}_2 + \text{H}_2\text{O} \rightarrow \text{WO}_2\text{OH} + \text{OH}
\]
Figure 1. Differential distribution curve of tungsten oxide particles

The surface of oxides is usually covered with a polymolecular layer of physically adsorbed water, which prevents modification. Therefore, the standard procedure preceding the modification consists in removing physically sorbed water, for which the oxide was subjected to heat treatment at 180 °C.

The energy dispersive interaction of the press powder of polyimide and highly dispersed modified WO$_2$ in a jet-vortex mill allowed for the activation of their surface, as well as high uniformity of distribution of the filler in the polyimide matrix and excluded the possibility of the formation of agglomerates.

The composite was pressed under a pressure of 200 MPa. When using such a high specific pressure, topochemical reactions between its components occur in the polymer composite, which in turn creates a strong connection between them and provides high strength characteristics of the developed composite.

The use of modified WO$_2$ made it possible to increase the degree of filling of the polymer composite by 15–20% as compared with unmodified tungsten oxide with the same strength of the composite.

Figure 2 shows the dependence of the relative increase in density on the pressing pressure for a polymer composite with a content of modified tungsten oxide from 50 to 80 wt.%.

Figure 2. Relative increase in the density of the polymer composite from the pressing pressure
With increasing filler content, the contribution of compaction pressure becomes more noticeable. Thus, for a composition containing 50% by weight of modified WO₂, the density in the studied molding interval changes by 2.3%, and starting with a pressure of ≈700 MPa, no changes are observed, and for a composition with a content of 80% by weight of filler, the density increase is already 16.0%. Obviously, with an increase in the content of modified WO₂, the degree of densification of the filler and the introduction of air with it make a greater contribution to the density of the obtained composite, which can also be a consequence of the high dispersion of modified WO₂. Thermoplastic polyimide matrix has a high creep, which affects the small change in the density of samples with 50% filling due to a better filling of the pores with the matrix at lower pressures. Also, at low fillings, the polymer's damping capacity makes a significant contribution.

4. Conclusion
Thus, the studies have shown the feasibility of a preliminary process of modifying a tungsten oxide-based powder filler in order to increase its compatibility with the polymeric polyimide matrix, which increases the density gain of the polymer composite by 16.0%.

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