# DEPOSITION OF $TiO_2$ COATINGS BY HIGH-VELOCITY AIR-GAS SUSPENSION PLASMA SPRAYING

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Experiments on deposition of $TiO_2$ coatings by using the $TiO_2$ water suspension containing 15 wt.% of the nanosized $TiO_2$ particles as a spraying material were carried out. The experiments were conducted by the high-velocity air-gas plasma spraying method (unit «Kiev-S»). Thickness of the deposited coatings was 80 ± 12 μm. The anatase/rutile content ratio changed during the spraying process from 79/21 (in powder) to 31/69 (in coating).

***Keywords:*** *titanium dioxide, suspension, coating, plasma spraying, phase composition, structure*

One of the trends in development of the thermal spraying methods is the use of suspensions consisting of a liquid phase and finely dispersed (up to nanosize) powder as a spraying material. This allows replacement of air transport of powders to the spraying zone by liquid transport and avoidance of such problems as poor flowability and sensitivity of finely dispersed powders to agglomeration. Also, this makes it possible to form thin (1 μm thick or thinner) layers of the spraying material, including with the nanosized structure [1, 2]. The experience accumulated up to now includes experimental studies on deposition of oxide ($Al_2O_3$–$TiO_2$, $ZrO_2$, $TiO_2$) and carbide (WC–Co) coatings [2]. Suspensions are sprayed by the plasma and flame spraying technologies [2] by using water and ethanol as a liquid medium.

The focus of researchers has been on deposition of coatings by using the $TiO_2$ suspension, which is associated with photocatalytic properties of the $TiO_2$ coatings and their high potential for purification of air (e.g. from acetylaldehyde, ammonia, nitrogen oxides etc.) and water (from phenols etc.) [3, 4]. It has been shown that the nanocrystalline porous $TiO_2$ layer forming in plasma spraying of the $TiO_2$ suspension can be used for manufacture of a new type of solar cells (Graetzel cells) characterised by an increased efficiency (10–11 %) [5].

The water suspension containing 15 wt.% of the nanosized $TiO_2$ particles was used as a source material for deposition of the $TiO_2$ coatings.

As revealed by X-ray phase analysis, the $TiO_2$ powder (Figure 1), which is a component of the suspension, contains 79 wt.% anatase (tetragonal lattice with elementary cell sizes $a$ = 0.3798 and $c$ = 0.9532 nm) and 21 wt.% rutile (tetragonal lattice with elementary cell sizes $a$ = 0.4595 and $c$ = 0.2955 nm).

The regions of coherent scattering for anatase and rutile estimated at 7.6 and 24 nm, respectively, are indicative of nanodispersion of the initial particles.

Examination of the powder with a scanning electron microscope shows that the $TiO_2$ particles with a size of about 100–200 nm form conglomerates up to 1.0–1.5 μm in size.

To provide uniform distribution of the powder particles in the suspension, prior to spraying it was subjected to ultrasonic treatment for 5–7 min by using the UZ-DN-A unit. It was enough to preserve homogeneity of the suspension for several hours and provide its uniform feed to the plasma jet.

The $TiO_2$ suspension coatings were deposited by the high-velocity air-gas plasma spraying by using the upgraded «Kiev-S» unit.

The suspension was transported to the plasma jet with an air compressor, which created the backup pressure by means of the compressed air in the suspension vessel. Prior to ignition of the plasma jet, the compressed air was fed under a low pressure via a separate line to the injector to blow the suspension feed nozzle. After ignition of the plasma jet and reaching the spraying mode by the plasmatron the suspension started to be fed from a low pressure of the backup

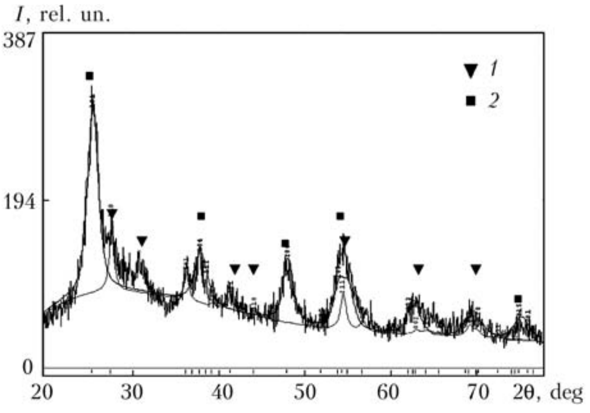


**Figure 1.** X-ray pattern of $TiO_2$ particles in initial suspension: *1* — rutile; *2* — anatase

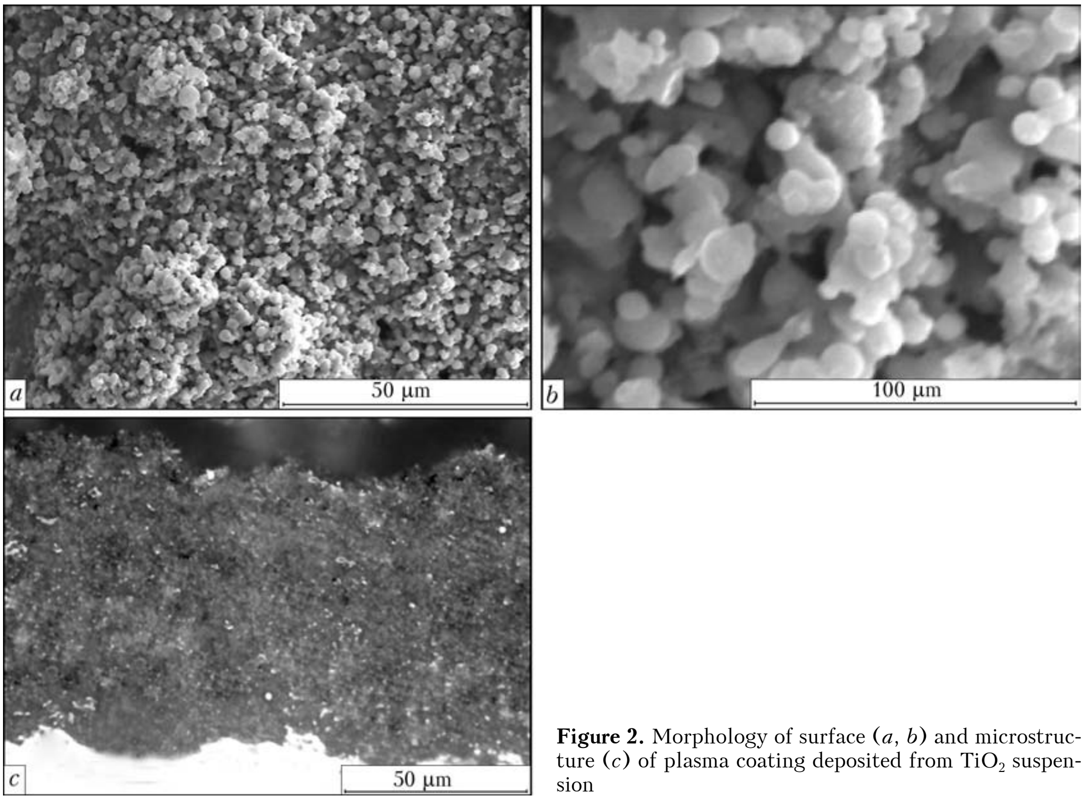

Figure 2. Morphology of surface ($a$, $b$) and microstructure ($c$) of plasma coating deposited from $TiO_2$ suspension

gas and, simultaneously, feeding of the compressed air for blowing the injector nozzle was stopped. Then the backup gas pressure mode was reached, when the suspension jet was fully mixed with the plasma jet causing no violation of its axial stability. The suspension was fed to under the plasmatron nozzle section at a distance of 10 mm and angle of 10° in a direction opposite to that of the plasma jet. Diameter of the injector nozzle was 0.5 mm.

Technological parameters of the unit after reaching the spraying mode were as follows: $I$ = 250 A, $U$ = = 290 V, $L$ = 120 mm, plasma gas flow rate — 18 m$^3$/h, and backup gas (air) pressure — 3.5 atm. The coatings were deposited on the carbon steel samples 16 × 16 × 3 mm in size.

Homogeneous coatings, uniform through thickness, crack-free and having no separation from the substrate, were produced as a result of the experiment (Figure 2). Thickness of the coatings was 80 ± 12 μm. They had a finely dispersed structure formed from rounded coagulated particles 6–17 μm in size. The coatings had low microhardness, i.e. 1420 ± 300 MPa, this being attributable to their low cohesion strength.

During spraying, heating of the powder by the plasma jet caused structural-phase transformations in titanium dioxide, leading to a change in proportion of its two main modifications — rutile and anatase. Thus, the content of anatase decreased to 31 wt.%, and that of rutile grew to 69 wt.%, compared to the initial powders with the anatase and rutile contents of 79 and 21 wt.%, respectively (see Figure 1). With this the lattice parameters of both phases changed but insignificantly: $a$ = 0.4593 and $c$ = 0.2942 nm for rutile, and $a$ = 0.3776 and $c$ = 0.9491 nm for anatase. Anatase is a low-temperature modification of $TiO_2$. In heating within a temperature range of 699–915 °C it transforms into rutile [6]. This explains increase in the rutile content of a coating during plasma spraying, compared to the initial powder.

Therefore, it was established that high-velocity plasma spraying of water suspension with the $TiO_2$ powder can provide formation of coatings up to 80–90 μm thick. As the catalytic activity of material of such a coating depends upon the content of the anatase phase in it, further efforts are aimed at finding the way of controlling the phase composition of the $TiO_2$ coatings produced by plasma spraying of the $TiO_2$ suspension, as well as at evaluation of the effect of the phase composition of the coatings on their catalytic activity or efficiency of using them for solar cells.

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