# Physicochemical properties of titanium nitride electric arc powder

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**Abstract**. Physicochemical properties of polymeric materials nano modifier on the basis of a titanium nitride powder synthesized at arc sputtering of the titan in a low pressure gas mix of nitrogen and an argon of are studied. It is shown, that particles have a nanometre size and a narrow grain size distribution. The questions connected with oxidation and recrystallization are discussed.

## 1. Introduction

The constant expansion of the areas of application of nanodispersed powders (NP) requires the study and development of methods for their preparation. It is especially important to find out the effect of dispersion of NP particles on their activity in such physicochemical processes as phase transformations, oxidation, sorption, etc. [1-4] The most interesting is the method of obtaining an NP by evaporation of a compact material using a low-pressure arc discharge and subsequent condensation of vapor-plasma flows in inert or reaction gas environments. This method allows one to obtain NPs of pure metals and their compounds with nitrogen and oxygen with a very narrow particle size distribution, with an average particle size of less than 10 nm [5].

The aim of this work is to study the physicochemical properties of titanium nitride nanowires obtained in a plasma of an electric low-pressure arc discharge.

## 2. Experimental

The starting powders were obtained by evaporation of titanium of technical purity using an electric arc discharge in a gas mixture of argon and nitrogen. The experimental setup and the dependence of the properties of the powder on the spraying conditions are discussed in detail in [6–8]. The morphological composition of the studied samples was studied using a JEOL JEM-2100 transmission electron microscope. The phase composition of the obtained samples was studied using an Advance D8 X-ray diffractometer in CuKα monochromatized radiation. The specific surface was measured by the BET method.

## 3. Results and discussion

Figure 1 shows a typical photograph of a sample. The powder is an ensemble of highly agglomerated particles of irregular shape from 5 to 10 nm in size. Formations up to 15 nm in size are also found, however, these are apparently agglomerates of smaller particles. Such agglomerates cannot be disaggregated. The study of particle size distribution showed that the obtained NP has a logarithmically normal distribution and an average particle size of 8 nm. Deviation from the average size is not more than 40%.

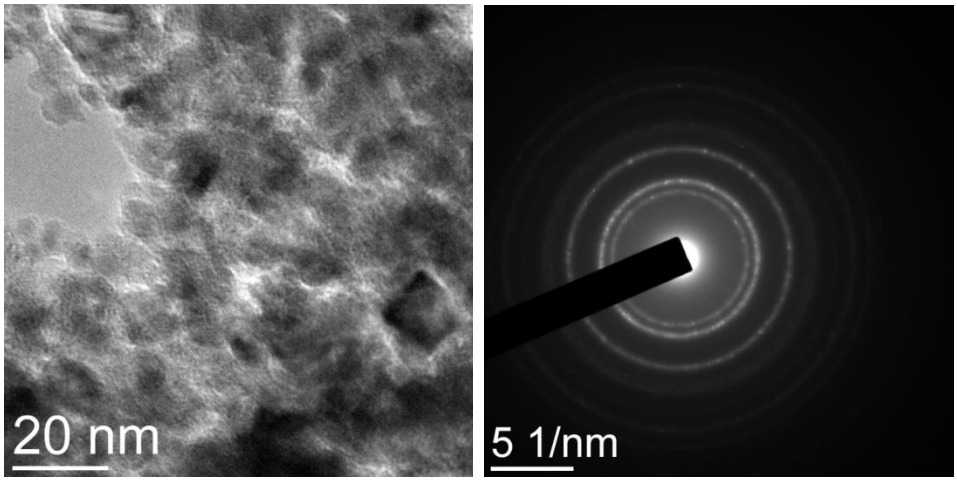


**Figure 1.** TEM image and electron diffraction pattern of titanium nitride NP obtained in a low-pressure arc discharge.

X-ray phase analysis showed (Figure 2) that the sample is a cubic phase of titanium nitride with a lattice parameter a = 0.4208 nm, which is significantly less than the parameter for standard TiN. The features of the shape of the peaks (narrow peaks against the background of wide ones) indicate the presence in the sample of two fractions that differ in crystallite size.

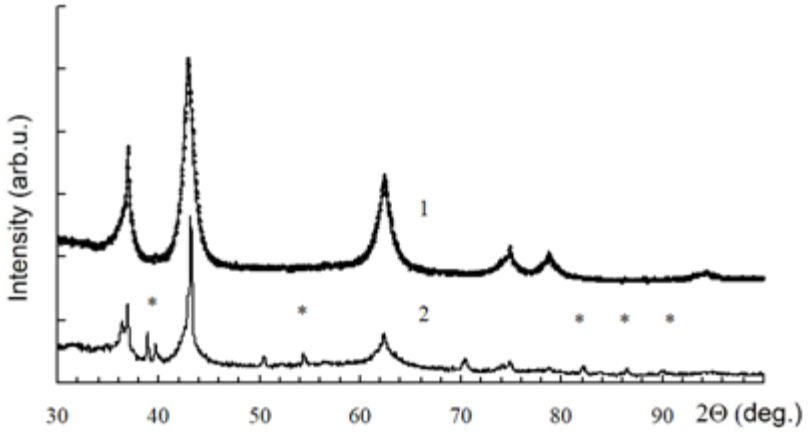


**Figure 2.** X-ray diffraction patterns of the sample: 1 — the experimental X-ray diffraction pattern of the initial sample is shown by dots, and calculated by a solid line; 2 is a radiograph of a sample heated to 543 K.

The specific surface was measured by the BET method. Its value calculated from the isotherm of low-temperature adsorption of argon was 546 $m^2$ / g. The value of the specific surface allows us to make an assumption that condensate of a much smaller size is deposited on the surface of the particles than the main powder. This condensate forms a rather porous "coat" around the particles and mainly determines the physicochemical activity of the powder.

Thermal analysis of the powder was carried out on a TG-DSC STA 409 PC Jupiter synchronous thermal analysis instrument. The weight of the sample was 100 mg. The sample was heated at a speed of 10 deg / min in the temperature range from 291 to 1273 K. The research results are shown in Fig. 3. In the temperature range from 333 to 443 K, intense evaporation of water occurs, as evidenced by a decrease in the mass of the sample by 9 wt. % (see thermogravimetric curve), although there is no pronounced minimum on the DTA curve. At a temperature of 536 K, a small exothermic effect is observed, which is not accompanied by a change in the mass of the sample. In the temperature range from 630 to 763 K, an insignificant increase in mass occurs (not more than 2 wt.%), Which is accompanied by a strong exothermic effect with a maximum at a temperature of 713 K. A further increase in temperature does not lead to noticeable thermal effects. Figure 2 (curve 2) shows the X-ray diffraction pattern of the sample heated to 543 K. In addition to cubic titanium nitride, reflections corresponding to the tetragonal $Ti_2N$ phase also appear in the sample.

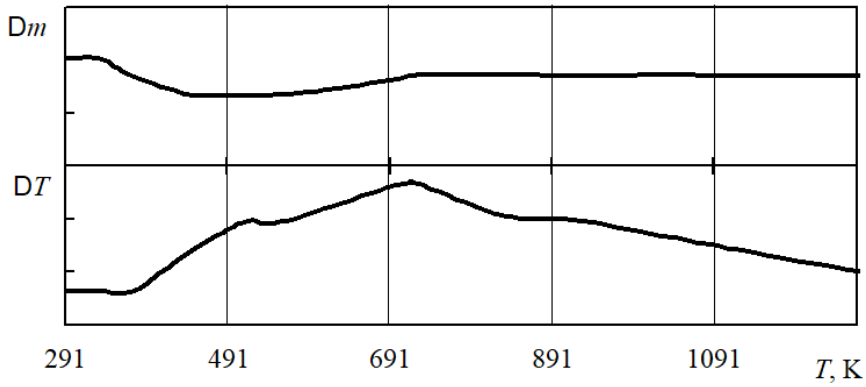


**Figure 3.** Thermogram of heating an electric arc titanium nitride powder.

When the sample is heated to a temperature of 800 K, titanium nitride is completely oxidized to $TiO_2$ with a tetragonal rutile lattice. The results of a study of the process of powder oxidation, obtained earlier [9], and electric arc powders are presented in Figure 4.

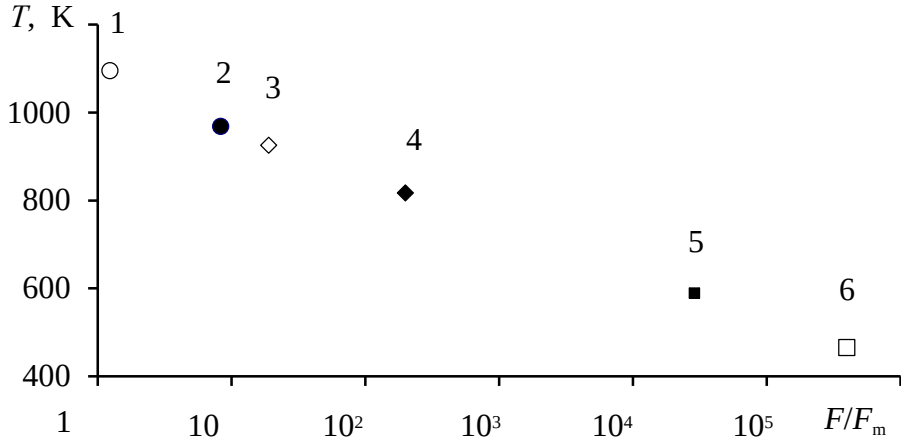


**Figure 4.** The temperature dependence of the onset of titanium nitride oxidation on the specific surface: 1 - crystals (size about 1 mm) obtained by hydrogen reduction of TiCl4 in a nitrogen plasma of a microwave discharge; 2, 3 - powders obtained by the method of self-propagating high-temperature synthesis; 4 - repeated nitriding of iodide metals; 5 - hydrogen reduction of metal chlorides in a nitrogen plasma of a microwave discharge; 6 - in a plasma of a low-pressure arc discharge.

As follows from Figure 4, the thermo-oxidative stability of the powders varies 3 times depending on the dispersion. Based on the obtained results of the behavior of electric arc titanium nitride in the temperature range from 443 to 713 K, we can conclude about two exothermic processes: recrystallization and oxidation. The oxidation process most likely occurs according to the mechanism proposed in [10], i.e. through the formation of oxynitride phases, which decompose with a further increase in temperature to form the rutile phase. Another feature of recrystallization is to maintain a significant deviation of the lattice parameter from the reference value. In [10–12], it was shown that nonequilibrium conditions for the production of nanopowders and their small sizes determine the presence of features in the crystal structure and imperfection in powder objects.

Deformation in particles can be the result of capillary forces, with the largest contribution to the mean square displacement being made by static displacements due to the inhomogeneous nature of the deformation in small particles. According to [13], it can be assumed that the most probable causes of lattice deformation of annealed titanium nitride are: insufficient completion of the crystal lattice formation process and, correspondingly, increased concentration of nonequilibrium vacancies due to the jump-like nature of crystallization; the effect of additional surface pressure due to the large contribution of surface energy to the total free energy of small particles, and structural deformations can be inhomogeneous in the particle's volume.

Thus, the following conclusions can be made.

1. Arc titanium nitride powders have an average particle size of 8 nm, the deviation from the average does not exceed 40%.

2. Non-stoichiometry of the metal in the powder is caused by its increased sorbing ability due to the large specific surface.

3. Powders have low oxidation resistance.

4. A significant decrease in the lattice parameter is caused by structural stresses inhomogeneous in particle size due to the size factor.

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