Particular Characteristics of the Synthesis of Titanium Nitride Nanopowders in the Plasma of Low Pressure Arc Discharge

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Annotation. The method of producing TiN nanopowders in the plasma of low pressure arc discharge in nitrogen atmosphere is discussed. The influence of gas pressure on nanopowder dispersion is studied. It is shown that the particles have nanometer size and a narrow particle size distribution.

Among the methods used to produce nanoscale powders [1-21], especially of refractory metals and their compounds, the most important place is given to the plasma technology, which provides high heating temperatures of a material and steep temperature gradients, so it is very attractive and technically simple method. The presence of supersaturated vapors of the initial compounds in the plasma and their high quench rate causes the formation of nanoparticles.

Recently the interest to the synthesis of nanomaterials (NM) based on refractory compounds, including titanium nitride, has increased. Various heating methods are used for the evaporation of material, such as laser, electron beams, etc.

In this work the arc evaporator, used in the process of TiN synthesis, had the following characteristics [22, 23]: a discharge current of 500 A, an intensity of the longitudinal magnetic field excited by the focusing coil on the surface of the cathode, of 80 Oe. Titanium of technical grade VT 1-00 was used as a cathode. In order to begin plasma chemical reactions, the chamber was preliminary evacuated to a pressure of 1 mPa and then it was filled by gaseous N_2. Evaporation was performed at two pressures of nitrogen: 0.1 Pa (TiN1 sample) and 10 Pa (TiN2 sample). Before evaporation the cathode was heated to 1200 K. Titanium nitride NP was accumulated for 10 minutes. TiN1 sample was of dark brown color, and TiN2 – of black color.

Morphological composition of NP was studied by scanning electron microscope JEOL JSM-7001F and transmission electron microscope JEM-2100 JEOL. Fig. 1 shows a typical picture of TiN1 sample. The powder includes particles of two types: spherical particles with size from 0.5 μm to 3 μm, wherein fine condensate dropped, and spherical particles ranging in size from 0.5 μm to 10 μm, which represent agglomerates of smaller particles of 0.1 μm order. The sample TiN2 for the electron microscopy studies was prepared as follows: the powder was placed in isopropyl alcohol and then it was dispersed in an ultrasonic bath for 2 minutes, and a solution drop was then placed on a carbon film substrate, located on an electron-microscopic supporting grid. The carbon film substrate was 10-15 nm thick. Fig. 2 shows a high-resolution electron microscopic image of TiN nanoparticles. The average particle size was 4 nm, some particles were up to 5-6 nm in size. TiN nanoparticles have a crystalline

structure, as evidenced by the atomic planes observed in the images. Particle shape was usually nearly spherical.

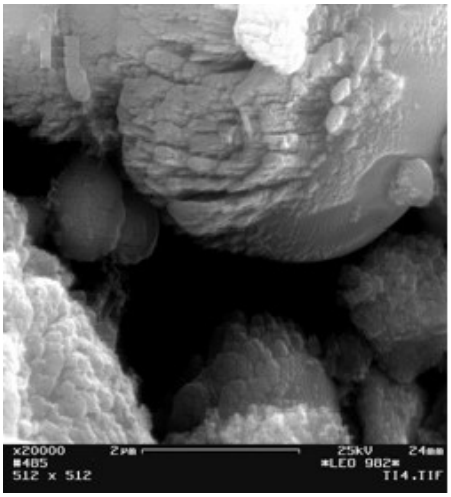

FIG. 1. SEM micrographs of TiN1 sample.

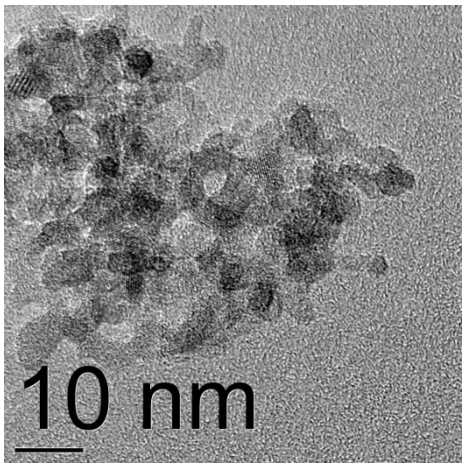

FIG. 2. TEM micrographs of TiN2 sample.

X-ray diffraction data were obtained using diffractometer Advance D8. CuKα monochromatic radiation was used. The scanning was carried out at room temperature in the angular range 30°-120° in 2θ with a step of 0.04°.

The X-ray pictures of the samples are shown in Fig. 3. The experimental X-ray picture of TiN2 sample and the estimated, obtained from full-profile adjustment, are given for comparison. The basic phase of the sample TiN1 is a cubic TiN with a lattice parameter a = 0.4242 nm. The lattice parameter is almost identical with the diffraction standards database ICDD-JCPDS-38-1420. There is a small amount of Ti_2N, the peaks of which are indicated by asterisks in Fig.3.

TiN2 sample represents a titanium nitride cubic phase with a lattice parameter of a = 0.4208 nm, which is substantially less than a lattice parameter of the standard TiN. The particularities of X-ray peaks showed the presence of two fractions in the sample, significantly different in crystallite size. This conclusion was based on the fact that the diffraction maxima have anomalously sharp peaks under the large integrated width. This

complex shape could be explained only by a superposition of two peaks, significantly different in width. Therefore, during a full-profile adjustment two fractions with different crystallite size and different composition percentage were introduced to the model. Full-profile adjustment of microstructural parameters revealed that the majority of the sample (~ 98%) is the fraction with an average crystallite size of 8 nm. The remaining 2% of the material consists of coarse fraction with grain size of > 150 nm.

The experimental results clearly indicate sufficient difference between powders obtained at various pressures of gas mixture. The structure of TiN1 sample is like the structure of the coatings obtained by the method of condensation and ion bombardment (CIB). The composition of the generated plasma in the working chamber is not uniform. In particular, upon evaporation from the surface of the titanium cathode, plasma state is formed comprising single, double or triply charged particles. Drop component and fragments of the cathode material may also present in the plasma in addition to the charged particles. The multicomponent character of plasma creates the conditions for the formation of condensate which is non-equilibrium in composition and structure. Fig. 3 shows that the X-ray reflexes are substantially widen. The analysis of widening revealed the presence of micro-tension and nanodispersed structure. Moreover, a greater contribution to line widening is due to defects and tensions in the powder structure. The estimated values of micro-tension in powders TiN1 and TiN2 are 0.8% and 0.6% respectively.

The authors of [24] pointed out that the basic process of nitrides formation occurs mainly on the substrate. Content of a non-metal in the condensate is a linear function of the energy of metal ions which are condensed on the substrate. The energy of the ions has its boundary value, at which a complete binding of the non-metal flow, dripped on the substrate, achieves. However, the work [24] does not consider the energy of electrons from the plasma of arc discharge, which can be considerable. Growth of condensate causes decrease of heat transfer to the substrate, and a determining factor in the process of nitrogen binding becomes a local overheating by the electron current. The other situation is observed in the processes of nitride formation under the pressures which make essential plasma phenomena. The electron microscopy of TiN2 sample shows that there are no large powder particles, such as represent in TiN1 sample. The size characteristics of crystallite TiN2 sample, obtained from full profile analysis of the diffraction patterns, are in good agreement with the results of microscopy and adsorption analysis.

It is known [25], the character and intensity of heat and mass transfer between the particles of the dispersed phase and the plasma flow are determined by energy content of the plasma flow, the physicochemical properties of the fine phase particles, nature of plasma-forming gas and, finally, the character of interaction between the plasma flow and fine dispersed phase, which mainly depends on the Knudsen criterion. When the plasma flow regime becomes molecular (Kn > 1), the convection processes are insignificant. Under these conditions, heat and mass transfer processes are most reasonable viewed from the standpoint of the kinetic theory. In this regard, the estimation of the possibility of evaporation of micro-droplet fraction particles in the plasma of arc discharge can be made due to the following fact: there is a flow of fast electrons in the cathode plasma and they are accelerated in an electrostatic field arising due to the ions which diffuse into the cathode side. The estimations show that the basic flow of heat from the plasma to the particle is due to the energy brought by the ions. The part of the energy brought by the electrons in the considered range of electronic temperature does not exceed 15%. The estimation of the time of complete evaporation of titanium particle with a diameter of 50 microns at an energy of the electrons of

about 3.5 eV and a plasma concentration of 10^{21} m^{-3} gave the value of 10^{-5} s, which is much less than the time while a particle of microdroplet fraction exists in the cathode region of the plasma, at a rate of its displacement not exceeding 100 m/s.

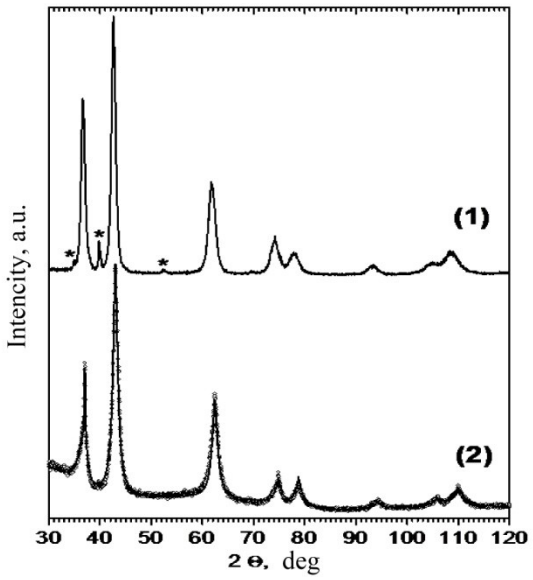

FIG. 3. X-Ray diffraction pattern of the TiN1 (*1*) and TiN2 (*2*).

Thus, the estimations show that, in condition of the sufficient energy content of the plasma flow, the process of cathode evaporation in low pressure arc discharge consists of two stages: firstly the cathode material is sprayed in a liquid phase in a cathode spot, and then is completely evaporated in a vapor-plasma flow. Furthermore, due to mixing of a metal vapor with a flow of ionized carrier gas, vapors are overheated, thus preventing premature condensation of the vapors and causes dissociation of already formed clusters. Uniform rate of flow cooling results in a very high size homogeneity of the resulting NM. Cooling the hot mixture by gas-dynamic expansion lets to achieve a rate of flow cooling of up to 10^7 K/s. It can be also assumed that a principal role in the processes of nitrides formation is played by plasma-chemical synthesis, i.e., titanium nitride formation directly in the plasma.

One of the possible mechanisms of droplet breaking is described in [26]. The industrial method for producing NM with additional breaking of particles is developed, its explanation reveals the essence of powders use. The method is based on electric arc spraying of metal in the atmosphere of a diatomic gas. In the powerful DC arc at atmospheric pressure metal droplets are formed, they are quickly saturated by almost completely dissociated gas - hydrogen or nitrogen. Upon cooling, the concentration of dissolved gas tends to the equilibrium one, defined by the Stiverts law. During a gassing process a drop breaks to a more dispersed state.

Thus, a dispersion of titanium nitride NM, produced in the plasma of low pressure arc discharge, depends on the gas pressure in the chamber. Increasing the pressure of the gas mixture leads to extremely high particle size uniformity of the produced NM and sharp decrease in the average size of particles.

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