Direct Dynamic Synthesis of Nanodispersed Titanium Nitride in Highvelocity Pulsed Electric-Discharge Plasma Jet[1]

A.A. Sivkov, A.S. Saigash, and A.J. Pak

Tomsk Polytechnic University, 30, Lenina ave., Tomsk, 634050, Russia
Phone: +8(3822) 56-36-82, E-mail: mpt@eltil.tpu.ru

Abstract – The paper describes the method for production of nanodispersed TiN in high-velocity electric-discharge plasma jet generated by the coaxial magnetoplasma accelerator. The process is realized in a short-term (~ 10^{-3} s) duty cycle of a titanium electrode accelerator. The basic material is generated by electric erosion off the acceleration channel (AC) surface. Depending on the density of the input energy dissipated in the AC, the powder particles may be spherical or irregular, 10–300 nm in size.

Hard and refractory compounds, such as titanium compounds (TiN, TiC, Ti_2CN, TiB_2, and others) with microhardness over 20 GPa, in the nanodispersed crystalline state can be basic material for the production of consolidated bulk ultra-hard materials (UHM) [1].

Hence, the development of new, simple and efficient methods of the direct synthesis of hard nanodispersed materials is very important today. The direct synthesis of nanodispersed crystalline materials in high-velocity pulsed dense electric-discharge plasma jet is one of such methods. The jet is generated in the high-current (about 10^5 A) pulsed coaxial erosion plasma accelerator (CPA) [2]. It is a conventional *Z*-pinch accelerator consisting of the central electrode (a steel rod 10–12 mm in diameter) and the barrel electrode with a cylindrical acceleration channel (AC) (a section of a steel tube 250 mm long, inner diameter up to 20 mm and the walls 2–5 mm thick). The accelerator is called "erosion" because the basic material for the synthesis of the desired product is generated by electric erosion off the cylindrical surface of the AC where the roots of the high-current fast *Z*-pinch discharge are moving. This system is able to work with any metals and alloys suitable for the production of electrodes of such geometry. Titanium is in every way one of the most "convenient" basic materials, and this factor brought about the research to carry out the dynamic synthesis of nanodispersed titanium nitride in gaseous nitrogen.

This is a direct and relatively simple method, as the process is fully realized in a short-term (~ 10^{-3} s) duty cycle of the CPA. The basic material (titanium) is generated by electric erosion off the AC surface and is captured in the melt by the fast discharge. At the temperature of several thousand degrees Celsius it converts to plasma state, accelerates to supersonic speed and ejects as a plasma jet from the AC to the cylindrical reactor chamber (0.31 m in diameter, 0.75 m long, 0.056 m^3 in volume) filled with commercially pure nitrogen at room temperature and close to atmospheric pressure.

An energy source for the CPA is a storage condenser with the capacitor bank C capacity up to $48 \cdot 10^{-3}$ F and charging voltage U_{ch} = 3–4 kV.

Dynamic parameters of the plasma jet while it was being formed in the nitrogen-filled reactor chamber were analysed from the photogram frames of the VFU-1 high-speed camera (Fig. 1).

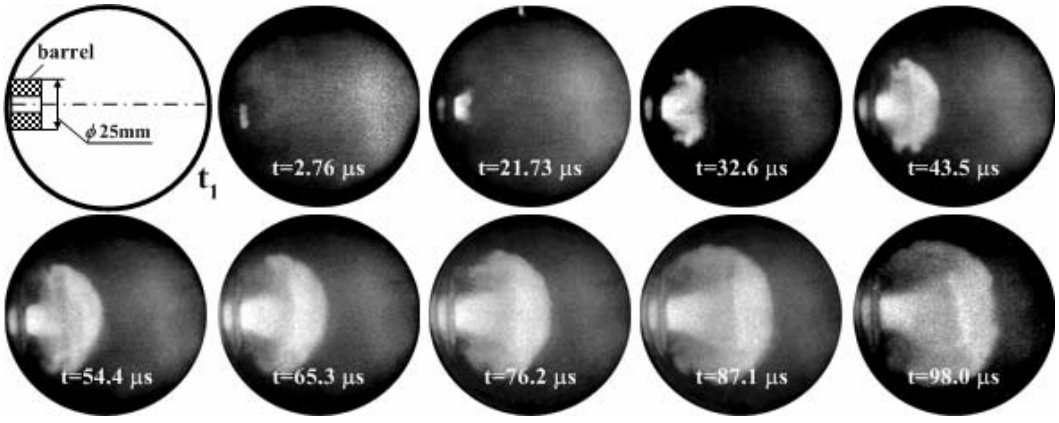

Fig. 1. Photogram of a supervelocity plasma jet flowing from the acceleration channel of the titanium barrel. Experimental conditions: $C = 48 \cdot 10^{-3}$ F, U_{ch} = 3.0 kV, W = 113 kJ, P = 1.0 atm; t_1 is the moment when plasma is coming out of the AC

[1] The study was performed with financial support of RFFI (Project No. 07-08-00804).

It can be seen in the pictures that the material tended to disperse more intensively at the front of the leading shock wave immediately at the first direct pressure shock with the matter rapidly cooling. It is apparently when the temperature was falling down that the conditions were created for plasmochemical synthesis of TiN. We reasonably suggested that the dispersivity of the desired product would depend on the jet energy and the efflux velocity – when these parameters increase, the particles get smaller.

One of the previous papers [3] has shown that when the AC geometry and electrode material are specified, the main factor determining the eroded mass m and the plasma flow velocity ϑ in the cross-section of the barrel is the value W of the input energy dissipated in the AC. Here, the specific value of electroerosive wear m/W was in direct proportion to the specific input energy W/V (V is AC volume). The input energy was determined through integration of the discharge power curve shown in current oscillogram $i(t)$ and voltage $U(t)$ on the CPA electrodes (Fig. 2).

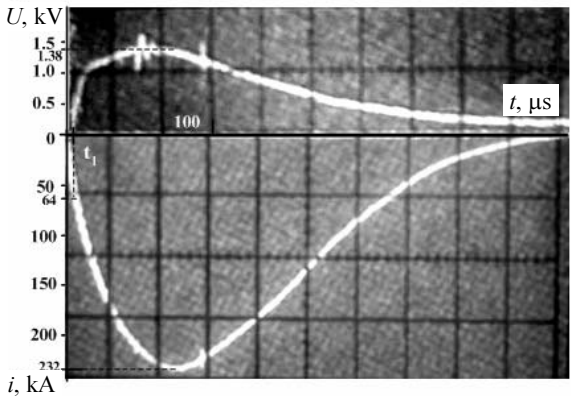

Fig. 2. Typical oscillograms of voltage on the electrodes $u(t)$ and operating current $i(t)$. Experimental conditions: $C = 48 \cdot 10^{-3}$ F, $U_{ch} = 3.0$ kV, $W = 113$ kJ, $P = 1.0$ atm

The mass m ejected from the AC was determined by weighing the barrel before and after the plasma shot.

The product of the dynamic synthesis was extracted at room temperature several hours after precipitation of the suspended fraction on the chamber walls.

The analysis of the smallest fraction, at least 50% of m was done by X-ray diffractometry (DRON-4 (FeK_α) and Shimadzu XRD6000 (CuK_α) diffractometers), scanning-electron (Philips SEM 515) and transmission (Philips SM 30) microscopes.

In each experiment a run of 3–4 plasma shots were carried out under the same conditions for each run. The input data and averaged product analysis results are detailed in the Table in descending order of values W, W/V, ϑ (experiments 1, 2, 3).

The microphotographs with various zoom degrees taken with a scanning-electron microscope show that the powder-like product synthesized in experiments 1, 2, and 3 were rather coarse agglomerates of small particles. It is important because agglomeration is a typical state for superdispersed powders obtained by electrophysical methods, electrical explosion of fine wires in particular [4]. The size and visually estimated density of agglomerates (Fig. 3, *a*) were decreasing as the input energy and jet velocity were stepping down. The photographs (Fig. 3, *b*) clearly show that rounded (spherical) lumps with powdery surface were indeed the clusters of very small particles. These particles grew considerably in size as the accelerator energy W and plasma flow velocity ϑ were falling down.

Table. Various conditions and averaged experimental data on production of TiN powder

No.	W, kJ	W/V, kJ/cm^3	P, atm nitrogen	m, g	ϑ, km/s	CSR area, nm	$D_{min} - D_{max}$, nm
1	113	1.2	1.0	16.7	3.5	30.0	10–200
2	81	1.0	1.0	12.6	3.2	40.0	25–250
3	70	0.8	1.0	33.9	2.0	90.0	30–300
4	100	1.2	2.0	14.4	–	25.0	10–150

At the same time, the most zoomed-in picture (Fig. 3, *c*) shows that the powder obtained in the experiment 3 consisted primarily of spherical particles, 30 to 300 nm in size with a small number of slightly bigger particles, approximately 400 nm in size. Scan patterns of powder-like products obtained in experiments 1, 2, and 3 (Fig. 3, *c*) did not allow to estimate the size of the particles; we could only see that the particles from experiment 1 were much smaller than those from experiments 2 and 3.

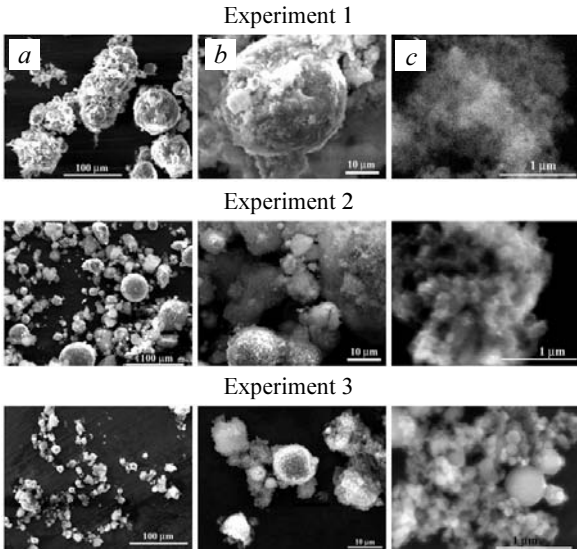

Fig. 3. Microphotographs of the dynamic synthesis powder-like products in the experiments 1, 2, and 3, Table; at different zooms

These empirical facts could be explained by the following: as the energy introduced into the discharge and the jet velocity were decreasing, the intensity

of the product dissipation inside the invariable volume of the reactor chamber was also falling down. The particles grew bigger in size, therefore, their specific surface area was decreasing. Here, when there was no forced circulation, the natural circulation was more intense in the case of a more high-energy shot. This factor, together with that of specific surface area provided for bigger agglomerates – smaller particles move faster and longer in the circulation flows, and are more likely to join the product agglomerates. The same tendency was observed when submicron powders were obtained by electroblasting at a strongly forced circulation of gaseous medium with suspended particles [4].

Figure 4 shows a typical diffraction pattern of a powder-like product obtained in one of the plasma shots in the experiment 2 (Table). The picture was taken with the DRON-4 (FeK_α) diffractometer with a nickel filter. The decoding and analysis of this and other similar diffraction patterns showed that the synthesized dispersed product was one and the same cubic TiN crystalline phase. The analysis of the physical broadening of diffraction reflections carried out using the full-profile analysis program PowderCell 2.4 showed that the area of coherent-scattering regions (CSR) in all the cases (Table) was from a few to dozens nm, which indicated that this powder-like product was nanodispersed. It is important that the CSR area clearly correlates with the W and ϑ values, i.e., when they were going down, CSR area was increasing.

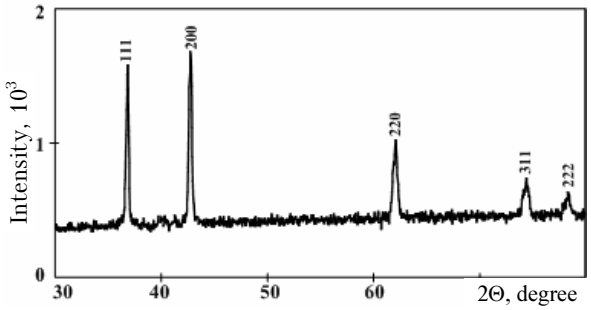

Fig. 4. X-ray diffraction pattern of the nanodispersed TiN powder with face-centered cubic arrangement

Even more convincing data on the sizes and geometry of TiN powder particles as well as additional information on their crystalline structure was produced by a transmission electron microscope and the analysis of diffraction patterns. The microphotographs in the Fig. 5, for example, show that at $W/V \geq 1.0$ kJ/cm^3 and average jet velocity $\vartheta > 3.0$ km/s (experiments 1 and 2) the powder particles were either round or irregular with natural faceting. The particles were, in general, up to 250 nm in size. Since the compactness of relatively equally-sized but differently shaped particles in the pictures is almost the same, we suggested that they represent one and the same crystalline phase – cubic TiN. This was confirmed by diffraction pattern analyses, electron-diffraction patterns of individual particles, in particular. The dark-field images of the particles are next to the bright-field image of the accumulation of particles. The electron-diffraction patterns also show diffraction reflections corresponding with the reflections from the surfaces (111), (200), (220) of the cubic lattice.

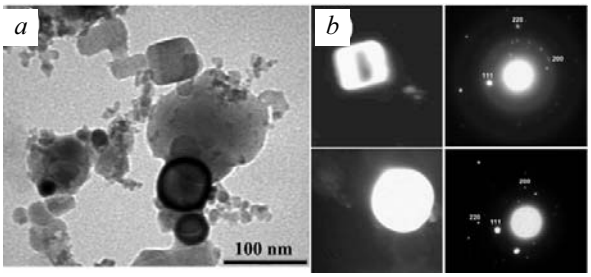

Fig. 5. Electronic microphotograph of nanodispersed powder (bright-field image) (*a*) and dark-field image of individual crystals with the corresponding electron diffraction patterns (*b*)

The halo on this electron-diffraction pattern points at the presence of an amorphized component of this phase or very small particles, about 1 nm in size. A shapeless buildup in the center of the bright-field image might be the accumulation of such particles (Fig. 5, *a*).

When specific energy was decreasing (experiment 3), smaller particles of spherical shape were formed (Fig. 3, *c*). Even smaller spherical TiN particles could be obtained at the maximum specific energy applied in this run of experiments but at the nitrogen pressure 2.0 atm (Fig. 6). The analysis of the experimental data showed that the shape of particles might depend on the rate of cooling and crystallization via gas phase. When the synthesis phase dispersed melt was cooled rapidly, small crystalline particles were formed. When the jet front velocity was decreasing, the crystallization of solid particles was slowing down, which helped form round particles. Besides, the cooling rate decrease could be caused by the temperature rise at the front of the leading shock wave and on the jet edge when external pressure was going up (experiment 4, Table).

The microphotographs obtained from the transmission microscope (Fig. 6) were used for the evaluation analysis of the dispersivity of powders synthesized under different conditions.

Figure 7 shows that the size distribution of particles was close to the normal logarithmic law [4]. It is important that particles were getting smaller in size as nitrogen pressure in the reactor chamber was increasing (experiment 4, Table).

According to the results of the experiments described above, the following conclusions were made:

1. The method based on the erosion CPA can be used for direct dynamic synthesis of titanium nitride nanodispersed powders with the cubic crystal lattice in the high-velocity electric discharge plasma jet. De-

pending on the specific input energy dissipated in the AC, the powder particles may be spherical or irregular.

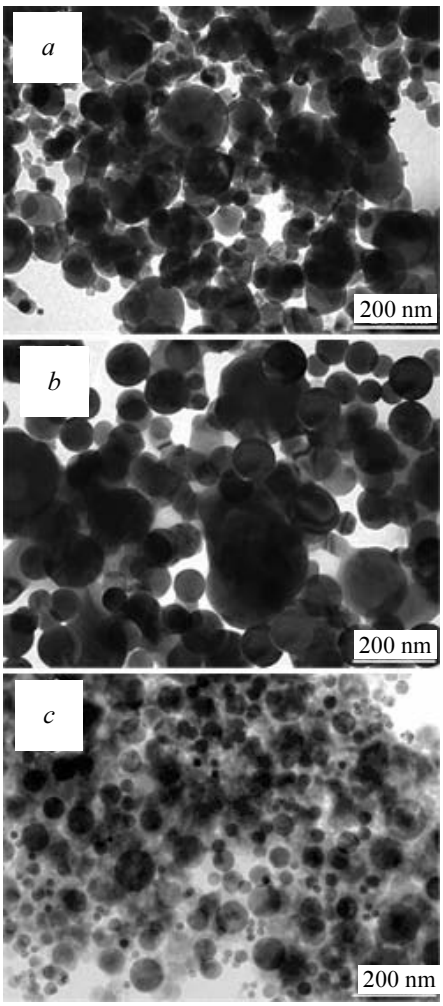

Fig. 6. Electronic microphotographs of nanodispersed powders obtained in the experiments 1 (*a*), 3 (*b*), and 4 (*c*), Table

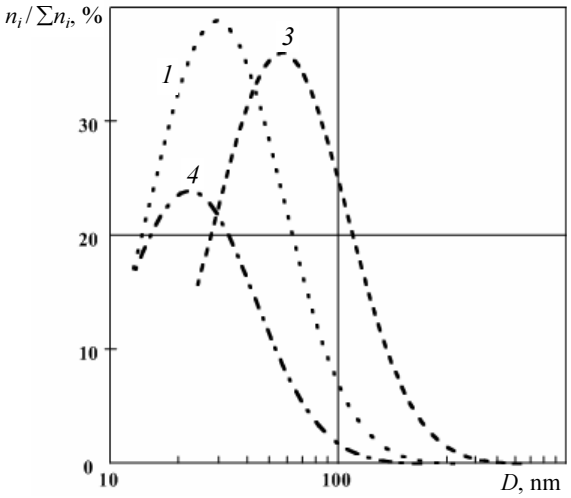

Fig. 7. Size distribution of particles, numbers correspond to the numbers of experiments in the Table

2. When there is no forced circulation of the gaseous medium in the restricted volume of the reactor chamber, TiN particles get smaller but their agglomerates grow in size as the input energy increases.

References

[1] R.A. Andriyevsky, *in Proc. Second All-Russian Nanomaterials Conf. "Nano-2007"; IV Int. Seminar "Nanostructural Materials-2007 Belarus–Russia"*, 2007, pp. 349.

[2] D.Yu. Gerasimov, A.A. Sivkov, and A.S. Saigash, *Patent RU 61856*, 2007.

[3] A.A. Sivkov, D.Yu. Gerasimov, and A.S. Tsybina, Elektrotekhnika **6**, 25–33 (2005).

[4] O.B. Nazarenko, *Electroblast nanopowders: production, properties, applications*, Tomsk, Publishing Department of Tomsk Polytechnic University, 2005, pp. 148.