NANOSYSTEMS:
PHYSICS, CHEMISTRY, MATHEMATICS

Avdeeva Yu.A., et al. *Nanosystems: Phys. Chem. Math.*, 2025, **16** (5), 628–639.
http://nanojournal.ifmo.ru
DOI 10.17586/2220-8054-2025-16-5-628-639

Original article

Formation of highly dispersed V–C–O–Ni and V–N–O–Ni compositions under low-temperature nitrogen plasma conditions

Yuliya A. Avdeeva[1,a], Irina V. Luzhkova[1,b], Aidar M. Murzakaev[2,c], Alexey N. Ermakov[1,d]

[1]Institute of Solid State Chemistry of the Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia

[2]Institute of Electrophysics of the Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia

[a]y-avdeeva@list.ru, [b]key703@yandex.ru, [c]aidar@iep.uran.ru, [d]ermakovihim@yandex.ru

Corresponding author: Yu.A. Avdeeva, y-avdeeva@list.ru

PACS 61.46.+w, 61.46.-w, 61.66.Fn

ABSTRACT Under conditions of plasma-chemical synthesis in low-temperature (4000-6000 °C) nitrogen plasma, ultrafine and nanocrystalline powder compositions VC–Ni and VN–Ni were obtained from mechanical mixtures containing vanadium carbide or nitride with metallic nickel in the ratio 1:1. X-ray studies have shown that the obtained plasma-chemical particles contain vanadium oxycarbides and oxynitrides, metallic nickel, and are also characterized by the presence of oxide phases of the V–O system. Electron microscopic studies of nanocrystalline fractions of VC–Ni and VN–Ni powder compositions using high-resolution transmission electron microscopy visualized the structure of the obtained particles. Using the fast Fourier transform, it was shown that the refractory components and metallic nickel form individual nanometer-scale particles that do not come into contact with each other. A chemical mechanism of the organization of highly dispersed mechanical mixtures V–C–O–Ni and V–N–O–Ni under conditions of quenching processes in a turbulent flow of nitrogen gas proceeding at a speed of 10^5 °C/s has been formulated on the basis of the performed research.

KEYWORDS vanadium carbide, vanadium nitride, nickel, plasma-chemical synthesis, X-ray phase analysis, high-resolution transmission electron microscopy

ACKNOWLEDGEMENTS The work was carried out in accordance with the state assignment for the Institute of Solid State Chemistry of the Ural Branch of the Russian Academy of Sciences (Theme No. 124020600024-5).

FOR CITATION Avdeeva Yu.A., Luzhkova I.V., Murzakaev A.M., Ermakov A.N. Formation of highly dispersed V–C–O–Ni and V–N–O–Ni compositions under low-temperature nitrogen plasma conditions. *Nanosystems: Phys. Chem. Math.*, 2025, **16** (5), 628–639.

1. Introduction

The formation of highly dispersed powder compositions based on refractory compounds of elements of subgroups IV–VIA of the Periodic Table is of interest when they are used as wear-resistant coatings for various purposes [1], or as insoluble modifying additives [2] in foundry production, ensuring the improvement of physical and mechanical characteristics.

Under these conditions, refractory compositions based on titanium carbides, nitrides and carbonitrides, where Ni or Co are used as the metal component [3,4], are most common in terms of production and practical application. They can be present in the form of independent particles, including those in the nanometer range, which can be realized through the use of milling technologies [5], or have the ability to form highly dispersed core-shell structures [6]. The core will be made up of refractory compounds, and the metallic phases will form the shell. The synthesis of highly dispersed "core-shell" structures is carried out under conditions of extreme impact methods, one of which is plasma-chemical technology in a low-temperature gas plasma [2].

It is known from the literature [7, 8] that vanadium carbides and nitrides (VC_x, VN_y) are similar in properties to titanium carbide-nitride compounds. Their melting and evaporation temperatures differ significantly. This undoubtedly affects the structural and morphological characteristics of the final synthesis products. Considering that the crystallization temperatures of VC and VN [9] are comparable with the boiling point of metallic nickel [10], the formation of highly dispersed particles with a "core-shell" structure can be greatly hampered or practically impossible according to [6]. Another characteristic feature of VC and VN can be a high tendency to oxidation with TiC and TiN [11].

The aim of this work is to produce and certify highly dispersed powder compositions based on vanadium carbide and nitride with the participation of metallic Ni obtained under conditions of plasma-chemical synthesis in low-temperature nitrogen plasma.

2. Methods

Highly dispersed powder compositions VC–Ni and VN–Ni were obtained by plasma-chemical synthesis in a low-temperature (4000 – 6000 °C) nitrogen plasma (GNIIKhTEOS, Moscow) described in [12].

Mechanical mixtures consisting of microcrystalline powders of VC or VN and Ni were immersed in a piston-type dispenser and fed at a rate of 200 g/h into a plasma-chemical reactor with a capacity of 25 kW. The plasma flow velocity was 55 m/s. After evaporation, the steam-gas mixture entered the quenching chamber, where condensation of the vapors occurred in the turbulent flow of the cooling gas, followed by the formation of highly dispersed VC–Ni and VN–Ni particles. Subsequently, the particles were moved by pneumatic flow to classifier 1 – a vortex-type cyclone, where the ultra-dispersed fractions of the obtained powder compositions were separated, and the nanocrystalline fractions were moved by pneumatic transport to classifier 2 – a bag-type filter.

Technical nitrogen was used as a plasma-forming gas and a cooling gas. The total gas consumption was 25 – 30 m^3/h, namely: 6 m^3/h – for plasma formation, 19 – 24 m^3/h – for hardening, stabilization and transportation.

Deactivation of highly dispersed powder products was carried out by slowly flowing air into the separation units of the plasma-chemical installation after synthesis.

As a result of plasma-chemical synthesis, two fractions of powder products VC–Ni and VN–Ni were obtained (classifier 1 – cyclone, classifier 2 – filter), differing in the morphology and phase composition of powder compositions with a core-shell structure.

The resulting powder compositions were studied by the X-ray diffraction method (Shimadzu XRD 7000, Japan, STOE Stady-P, Germany, 2Θ = 5 – 80° with exposure of 1 – 20 s per point). The presence of free carbon was investigated by Raman spectroscopy (Renishaw inVia Reflex). The density of the formed highly dispersed mechanical mixtures was determined using an AccuPyc II 1340 V1.09 helium pycnometer. The specific surface area was determined in accordance with the BET method (Gemini VII 2390 V1.03 (V1.03 t) specific surface area analyzer).

Based on the density data and the BET method, in accordance with formula (1) [13], the calculated values of the average particle size of all fractions obtained were determined.

$$d = \frac{6}{S_{sp}\rho}, \tag{1}$$

where d is the average particle diameter, S_{sp} is the specific surface area, ρ is the density.

To confirm the highly dispersed state, the nanocrystalline components of the powder composites from the filter were studied using high-resolution transmission electron microscopy (HRTEM) (JEOL 2100, Japan).

3. Results and discussion

Experimental data from X-ray phase analysis, density measurements, specific surface area by the BET method and calculated values of the average particle size for highly dispersed VC–Ni and VN–Ni compositions are given in Table 1.

According to the X-ray phase analysis data, the highly dispersed composition extracted from the cyclone (Table 1, No. 1, Fig. 1), which was obtained from a mechanical mixture of vanadium carbide VC and metallic Ni in a ratio of 1:1, contains 37 wt.% of vanadium oxycarbide $VC_{0.78}O_{0.07}$ (sp. gr. Fm-3m) [14], 20 wt.% of metallic Ni (sp. gr. Fm-3m), tetrahedral (sp. gr. P42/mnm) and rhombohedral (sp. gr. R-3c) vanadium oxides VO_2 (9 wt.%) and V_2O_3 (12 wt.%), respectively. 6 wt.% of titanium-nickel nitride $TiN_{0.84}O_{0.11}$ (sp. gr. Fm-3m) [14], 1 wt.% of titanium-nickel nitride $Ti_{0.7}Ni_{0.3}N$ (sp. gr. P-6m2) [15] and carbon C of rhombohedral (sp. gr. R-3m, 9 wt.%) and hexagonal (sp. gr. P63/mmc, 6 wt.%) modifications were recorded as impurity phases.

The presence of oxygen-containing phases $VC_{0.78}O_{0.07}$, VO_2 and V_2O_3 in the overcondensed VC–Ni system is associated with the processes of deactivation of the final product. The presence of oxynitride $TiN_{0.84}O_{0.11}$ and titanium-nickel nitride $Ti_{0.7}Ni_{0.3}N$ is due to the fact that powdered titanium nickelide TiNi was used during the preliminary cleaning of the plasma-chemical installation, which, under the conditions of plasma-chemical synthesis in nitrogen plasma, forms highly dispersed powder compositions with a core-shell structure of the TiN–Ni composition [16]. Considering that complete titanium nitrides, in accordance with [10], are not wetted by metal melts, the recondensed highly dispersed particles contain refractory titanium nitride cores covered with a $Ti_{0.7}Ni_{0.3}N$ buffer layer and a Ni metal shell [17]. Condensation of free carbon occurs because the boiling and crystallization temperatures [18] significantly exceed those for VC, allowing the formation of a nucleus, on which vanadium carbide settles during condensation of the evaporated mechanical mixture of VC–Ni in the quenching chamber.

The recondensed fraction of the mechanical mixture VC–Ni from the bag-type filter (Table 1, No. 2, Fig. 1), according to X-ray diffraction data, contains 21 wt.% of $VC_{0.568}N_{0.398}$ (sp. gr. Fm-3m) [14], 26 wt.% of Ni (sp. gr. Fm-3m), 52 wt.% of V_2O_3 (sp. gr. R-3c) and 1 wt.% of $Ti_{0.7}Ni_{0.3}N$ (sp. gr. P-6m2). The formation of vanadium carbonitride $VC_{0.568}N_{0.398}$ is due to the fact that during the recondensation process, as shown on the example of work [19], at the crystallization stage two types of particles are formed in the quenching chamber of the plasma-chemical installation. Particles of the first type are formed from the evaporated initial components, where the refractory core is a "carbide – carbonitride" composition. Such particles subsequently settle in a vortex-type cyclone during separation. The second type of particles is formed on the basis of unevaporated residues of the initial refractory particles. In this case, the refractory

TABLE 1. Physico-chemical characteristics of highly dispersed powder compositions VC–Ni and VN–Ni obtained during plasma-chemical synthesis in a low-temperature nitrogen plasma of mechanical mixtures of vanadium carbide or nitride with nickel (1:1)

No.	Fraction	Phase composition, wt. %, a, b, c, nm	ρ, g/cm^3	S_{sp}, m^2/g	d, μm
1	VC–Ni (cyclone)	37 % $VC_{0.78}O_{0.07}$ (sp. gr. Fm-3m), $a = 0.415(2)$ 20 % Ni (sp. gr. Fm-3m), $a = 0.350(0)$ 9 % VO_2 (sp. gr. P42/mnm), $a = 0.455(0)$, $c = 0.286(3)$ 12 % V_2O_3 (sp. gr. R-3c), $a = 0.495(4)$, $c = 1.398(3)$ 6 % $TiN_{0.84}O_{0.11}$ (sp. gr. Fm-3m), $a = 0.424(2)$ 1 % $Ti_{0.7}Ni_{0.3}N$ (sp. gr. P-6m2), $a = 0.294(1)$, $c = 0.289(0)$ 9 % C (sp. gr. R-3m), $a = 0.249(6)$, $c = 1.013(0)$ 6 % C (sp. gr. P63/mmc), $a = 0.242(0)$, $c = 0.694(0)$	3.99	12.40	0.12
2	VC–Ni (filter)	21 % $VC_{0.568}N_{0.398}$ (sp. gr. Fm-3m), $a = 0.415(1)$ 26 % Ni (sp. gr. Fm-3m), $a = 0.350(8)$ 52 % V_2O_3 (sp. gr. R-3c), $a = 0.494(5)$, $c = 1.391(7)$ 1 % $Ti_{0.7}Ni_{0.3}N$ (sp. gr. P-6m2), $a = 0.294(4)$, $c = 0.290(9)$	3.22	59.10	0.03
3	VN–Ni (cyclone)	28 % VN (sp. gr. Fm-3m), $a = 0.413(8)$ 3 % VC (sp. gr. Fm-3m), $a = 0.416(6)$ 32 % Ni (sp. gr. Fm-3m), $a = 0.350(7)$ 12 % TiN (sp. gr. Fm-3m), $a = 0.424(3)$ 1 % $Ti_{0.7}Ni_{0.3}N$ (sp. gr. P-6m2), $a = 0.293(9)$, $c = 0.289(4)$ 16 % C (sp. gr. P63mc), $a = 0.245(9)$, $c = 1.340(5)$ 6 % Si (sp. gr. Fd-3m), $a = 0.542(6)$ 2 % Fe (sp. gr. Im-3m), $a = 0.286(5)$	5.14	9.80	0.12
4	VN–Ni (filter)	61 % $VN_{0.82}O_{0.14}$ (sp. gr. Fm-3m), $a = 0.414(0)$ 16 % V_2O_3 (sp. gr. R-3c), $a = 0.498(7)$, $c = 1.389(1)$ 23 % Ni (sp. gr. Fm-3m), $a = 0.351(7)$	4.20	59.60	0.02

cores will be a “carbonitride – nitride” composition, and the highly dispersed particles formed on their basis will settle on a bag-type filter. As in the previous case, the powder composition contains metallic Ni of cubic modification and hexagonal titanium-nickel nitride $Ti_{0.7}Ni_{0.3}N$. Its formation is due to the presence of nitride TiN, the determination of which by X-ray methods is difficult because of the isomorphism of refractory carbide-nitride compounds of titanium and vanadium and the nanocrystalline state of the sample (Table 1 No. 2, Fig. 1).

The next stage of the experimental work was the certification of highly dispersed compositions obtained from a mechanical mixture of powdered vanadium nitride VN with metallic Ni in a ratio of 1:1. It should be noted that the installation was not cleaned after recondensation of the mechanical mixture VC–Ni. In this regard, the phase composition of the recondensed powder composition VN–Ni from the cyclone can be described by the presence of compounds presented in Table 1 No. 3.

The formation of VN (28 wt.%, sp. gr. Fm-3m) and Ni (32 wt.%, sp. gr. Fm-3m) is regulated by the composition of the mechanical mixture. The presence of vanadium carbide VC (3 wt.%, sp. gr. Fm-3m), titanium nitride TiN (12 wt.%, sp. gr. Fm-3m), titanium-nickel nitride $Ti_{0.7}Ni_{0.3}N$ (1 wt.%, sp. gr. P-6m2) can be explained by the presence of impurities from previous experiments. The presence of 6 wt.% of Si (sp. gr. Fd-3m) is due to the fact that the main purpose of the plasma-chemical unit is to obtain powder silicon on a semi-industrial scale. The formation of free carbon C (sp. gr. P63mc), which in this case is an impurity element, is described above. The presence of iron Fe (2 wt.%, sp. gr. Im-3m) is a characteristic feature of the plasma-chemical synthesis technique since all units are made of steels of different grades.

The recondensed fraction of VN–Ni powder from the filter contains 61 wt.% of $VN_{0.82}O_{0.14}$ (sp. gr. Fm-3m), 16 wt.% of V_2O_3 (sp. gr. R-3c), 23 wt.% of Ni (sp. gr. Fm-3m). The presence of oxygen-containing compounds in this composition is explained above.

To clarify the phase composition of refractory cores, all powder compositions were subjected to chemical etching in a boiling solution of concentrated HCl. The etching time was 60 min.

The results of X-ray phase analysis of the etched compositions are given in Fig. 2(a,b) and in Table 2.

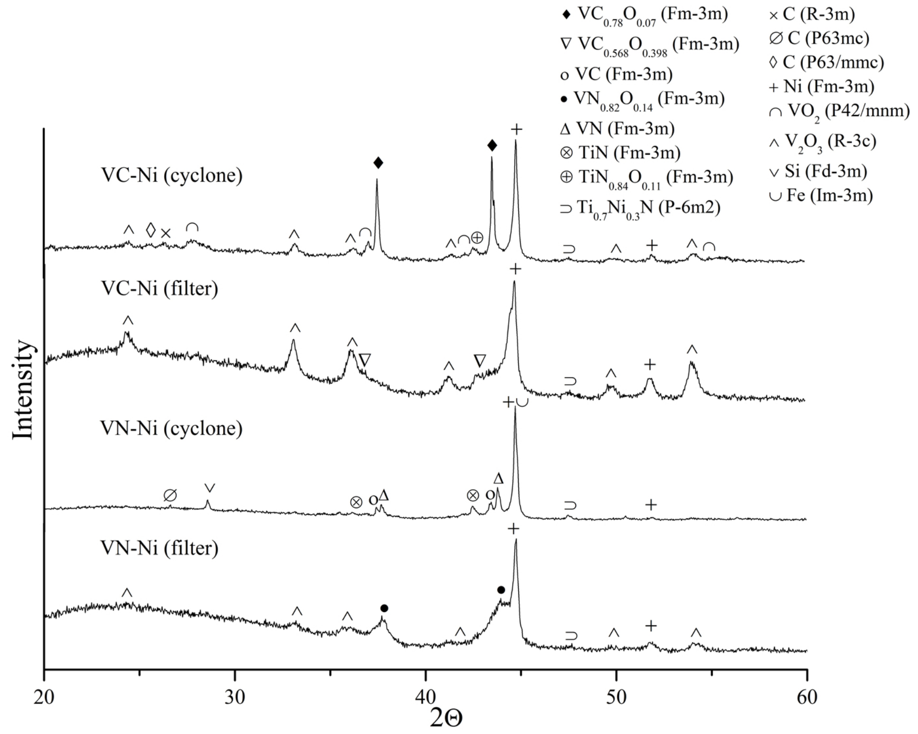
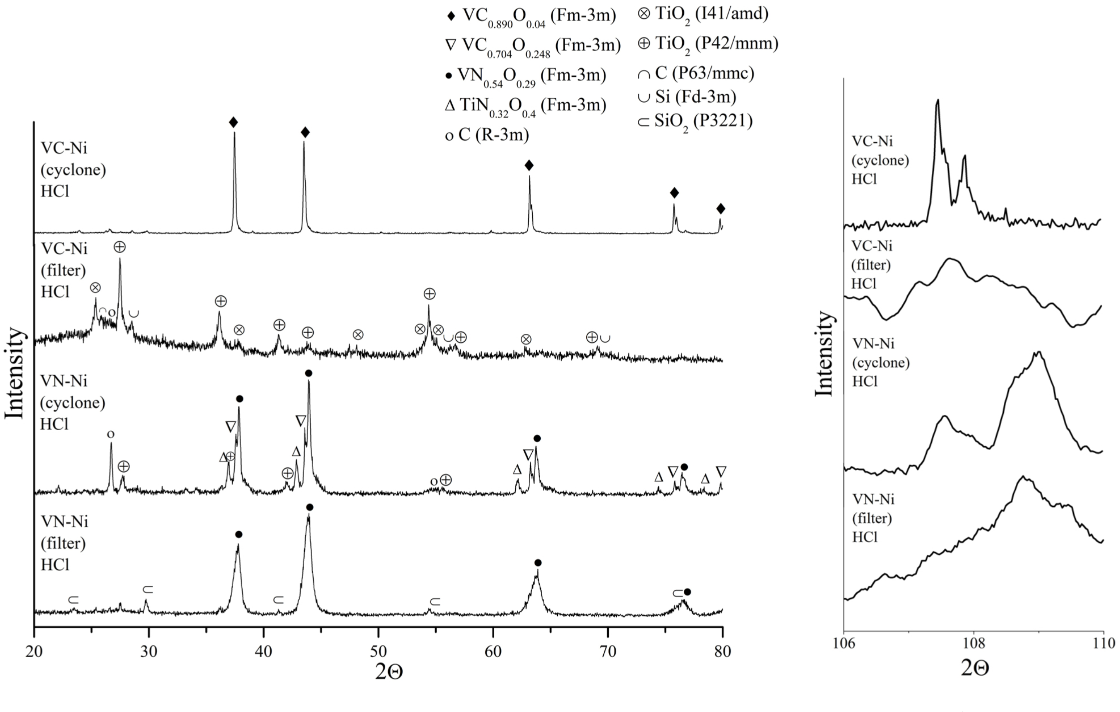


FIG. 1. X-ray diffraction patterns of highly dispersed VC–Ni and VN–Ni powder compositions obtained during plasma-chemical synthesis in low-temperature nitrogen plasma



(a) (b)

FIG. 2. Results of X-ray phase analysis of VC–Ni and VN–Ni powder compositions obtained during plasma-chemical synthesis after etching in HCl in the ranges of 2Θ = 20 – 80° (a) and 106 – 110° (331) (b)

TABLE 2. Physicochemical characteristics of highly dispersed powder compositions of VC–Ni and VN–Ni obtained during plasma-chemical synthesis after etching in HCl

No.	Fraction	Phase composition, wt.%, a, b, c, nm	Composition of the refractory phase [14] along line (331)
1	VC–Ni (cyclone) HCl	100 % $VC_{0.890}O_{0.040}$ (sp. gr. Fm-3m), $a = 0.417(3)$	$VC_{0.860}O_{0.060}$, $a = 0.416(3)$ nm $VC_{0.704}N_{0.248}$, $a = 0.415(4)$ nm
2	VC–Ni (filter) HCl	23 % C (sp. gr. R-3m), $a = 0.247(9)$, $c = 1.010(9)$ 16 % C (sp. gr. P63/mmc), $a = 0.242(0)$, $c = 0.689(9)$ 9 % Si (sp. gr. Fd-3m), $a = 0.542(7)$ 15 % TiO_2 (sp. gr. I41/amd), $a = 0.377(8)$, $c = 0.952(1)$ 37 % TiO_2 (sp. gr. P42/mnm), $a = 0.459(1)$, $c = 0.295(8)$	
3	VN–Ni (cyclone) HCl	11 % $VC_{0.704}O_{0.248}$ (sp. gr. Fm-3m), $a = 0.415(4)$ 47 % $VN_{0.540}O_{0.290}$ (sp. gr. Fm-3m), $a = 0.412(1)$ 10 % $TiN_{0.320}O_{0.400}$ (sp. gr. Fm-3m), $a = 0.422(0)$ 24 % C (sp. gr. R-3m), $a = 0.248(3)$, $c = 1.001(4)$ 8 % TiO_2 (sp. gr. P42/mnm), $a = 0.455(5)$, $c = 0.286(9)$	$VC_{0.82}O_{0.04}$, $a = 0.416(3)$ nm $VC_{0.704}N_{0.248}$, $a = 0.415(4)$ nm $VC_{0.57}O_{0.29}$, $a = 0.413(2)$ nm $VN_{0.56}O_{0.38}$, $a = 0.412(8)$ nm $VN_{0.56}O_{0.29}$, $a = 0.412(3)$ nm
4	VN–Ni (filter) HCl	85 % $VN_{0.540}O_{0.290}$ (sp. gr. Fm-3m), $a = 0.412(1)$ 15 % SiO_2 (sp. gr. P3221), $a = 0.435(2)$, $c = 0.497(0)$	$VN_{0.56}O_{0.38}$, $a = 0.412(8)$ nm

X-ray studies have shown that the etched recondensed composition based on vanadium carbide VC from the cyclone (Fig. 2(a), Table 2 No. 1) contains vanadium oxycarbide, which, in accordance with [14], is close to the composition $VC_{0.890}O_{0.040}$. Additionally, for a more thorough study of the composition, it is possible to present the results of X-ray phase analysis carried out based on the results of shooting of the etched sample at large angles (2Θ = 106 – 110°) (Fig. 2(b)). First of all, it should be noted that at first glance, the reflection (331) is decomposed into $K_{\alpha1}$- and $K_{\alpha2}$-components. However, according to the literature data [20–22], the processes of evaporation and condensation occurring under the conditions of plasma-chemical synthesis are non-equilibrium. This entails the absence of a homogeneous state of the obtained products. Under these conditions, a detailed study of the double reflections (311) showed that the etched refractory base is represented by two components, namely, oxycarbide $VC_{0.860}O_{0.060}$ and carbonitride $VC_{0.704}N_{0.248}$, which have similar unit cell parameters given in [14].

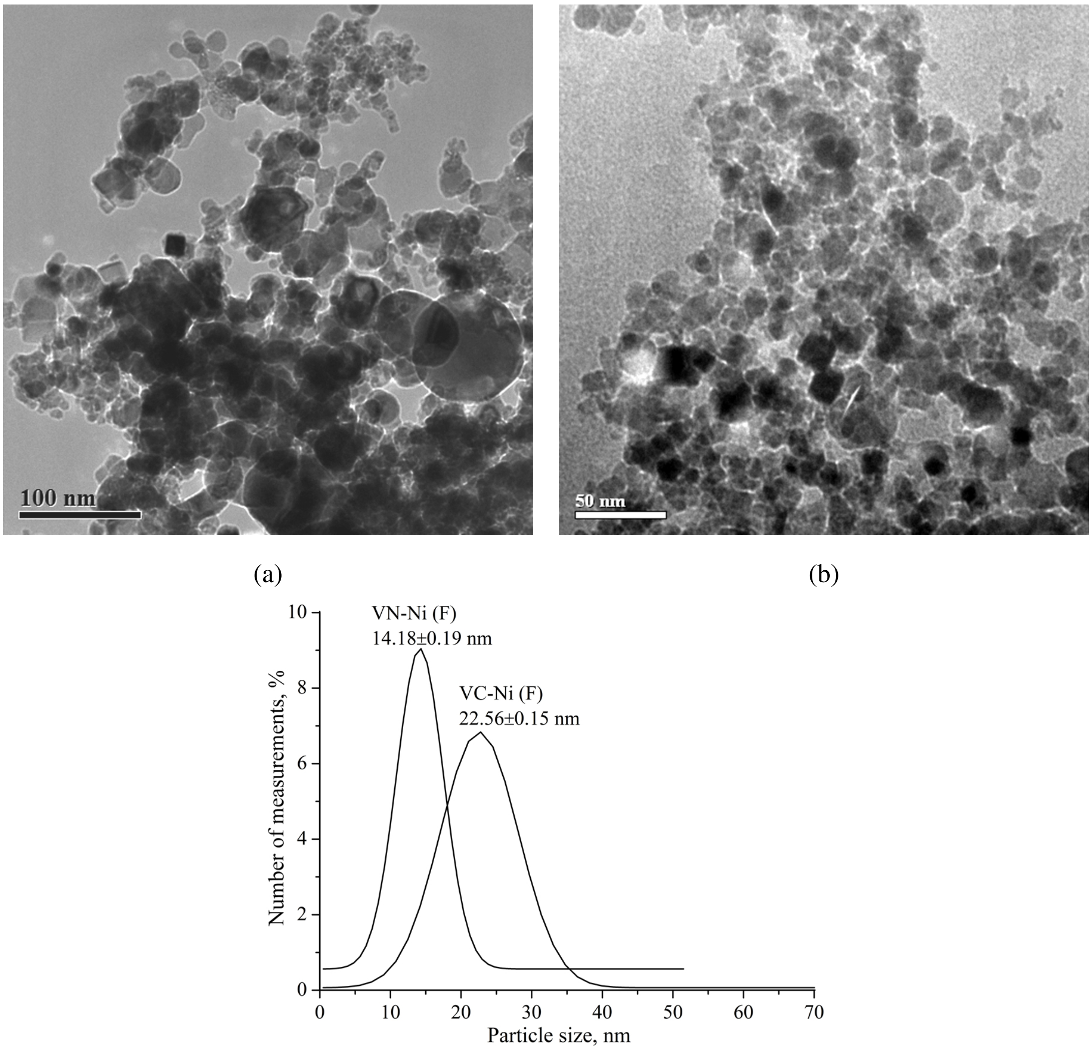
The X-ray diffraction pattern of the highly dispersed VC–Ni powder composition (filter fraction) after etching in HCl reveals the presence of oxide phase components in the form of two modifications of C, rutile and anatase forms of TiO_2 and cubic form of Si, shown in Fig. 2(a) and in Table 2 No. 2. The absence of refractory vanadium compounds can be explained by the fact that during the boiling process, all phase components containing vanadium and being in a nanocrystalline state, completely dissolved. Nanocrystalline particles containing vanadium carbide are significantly susceptible to oxidation during long-term storage. This subsequently suggests intensive decomposition in a boiling solution of concentrated HCl, as was shown in a number of studies [23]. The correctness of these judgments is confirmed by the presented image of the X-ray diffraction pattern in the angle interval 2Θ = 106 – 110 °, in which the (331) reflection is absent.

Etching of the VN–Ni fraction from the cyclone in a solution of boiling concentrated HCl showed that, according to the results of chemical reactions, based on X-ray data (Fig. 2(a), Table 2 No. 3), cubic $VC_{0.704}O_{0.248}$, $VN_{0.540}O_{0.290}$, $TiN_{0.320}O_{0.400}$ [14], rhombohedral C and TiO_2 in the form of rutile are present. Identification of the X-ray pattern taken in the angle interval 106 – 110° (Fig. 2b, Table 2 No. 3) shows that, as in the previous case with the etched recondensed mechanical mixture of VC and Ni (fraction from the cyclone) (Fig. 2a, b, Table No. 1), the reflections (331) for VC and VN are doubled. After determination of the unit cell parameters, it can be said that upon etching in boiling HCl, cubic oxycarbides $VC_{0.82}O_{0.04}$ ($a = 0.416(3)$ nm), $VC_{0.704}N_{0.248}$ ($a = 0.415(4)$ nm), $VC_{0.57}O_{0.29}$ ($a = 0.413(2)$ nm) and oxynitrides $VN_{0.56}O_{0.38}$ ($a = 0.412(8)$ nm), $VN_{0.56}O_{0.29}$ ($a = 0.412(3)$ nm) are present [14]. Cubic titanium oxynitride $TiN_{0.320}O_{0.400}$ acts as a refractory impurity phase, the (311) reflection of which overlaps with oxynitride phases. Carbon C (sp. gr. R-3m) and rutile TiO_2 are also included in the etched composition.

The recondensed fraction from the filter, etched for 1 hour in boiling concentrated HCl, obtained as a result of plasma-chemical synthesis of the mechanical mixture VN–Ni, according to the X-ray diffraction data in Fig. 2(a), Table 2 No. 4, contains cubic titanium oxynitride $VN_{0.540}O_{0.290}$ and hexagonal SiO_2 (sp. gr. P3221). A detailed study of the (311) reflection in the angle interval 2Θ = 106 – 110° (Fig. 2(b), Table 2 No. 4) shows that it corresponds to the composition of the oxynitride $VN_{0.56}O_{0.38}$ ($a = 0.412(8)$ nm).

To determine the presence and localization of phase components determined by X-ray diffraction, the nanocrystalline components of the powder fractions from the filter were studied using high-resolution transmission electron microscopy (Figs. 3–6).

First of all, it should be noted that the average particle size (Fig. 3(a-c)), according to the results of direct measurements, was 22.56 ± 0.15 nm for the fraction from the VC–Ni powder filter and 14.18 ± 0.19 nm for a similar fraction of VN–Ni powder.



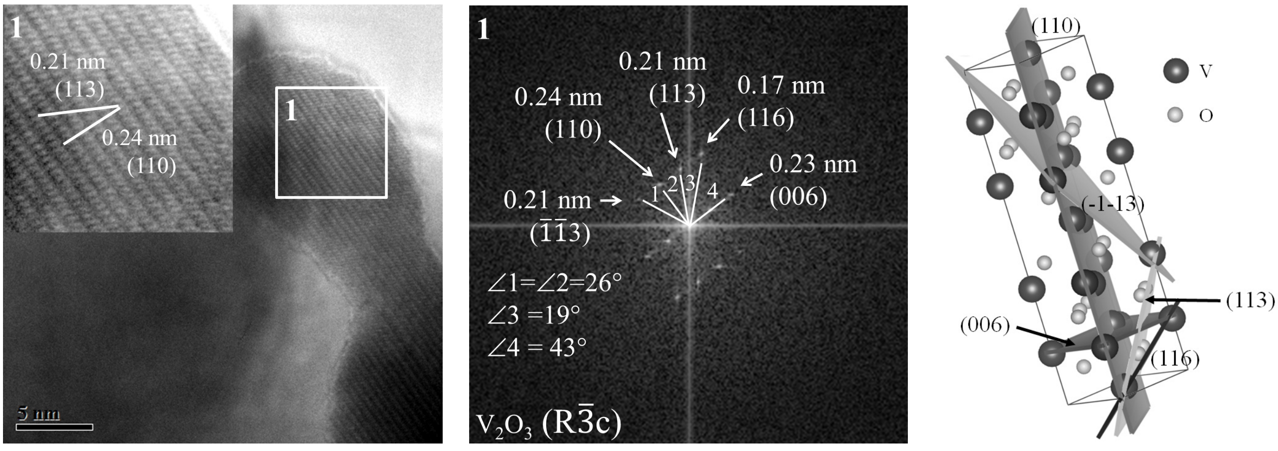
(a) (b)

(c)

FIG. 3. Electron microscopic images of nanocrystalline components of plasma-chemical compositions VC–Ni (a), VN–Ni (b) and particle distribution histograms (c)

Figure 4(a) shows a nanocrystalline VC–Ni particle, on which vanadium oxide V_2O_3 of rhombohedral modification (sp. gr. R-3c) is present, interpreted based on the FFT results (Fig. 4(b)) of section 1 (Fig. 4(a)). In particular, $d_{(-1-13)} =$ 0.21 nm; $d_{(113)} = 0.21$ nm; $d_{(110)} = 0.24$ nm; $d_{(116)} = 0.17$ nm; $d_{(006)} = 0.23$ nm are determined on the FFT. The correctness of the interpretation of the rhombohedral vanadium oxide V_2O_3 is confirmed by the similarity of the intersection angles of planes in the FFT picture (Fig. 4(b)) and the theoretical model of the V_2O_3 lattice shown in Fig. 4(c).

The presence of nanocrystalline Ni particles in the VC–Ni composition is shown in Fig. 5. Based on the results of microscopic studies taking into account FFT transformations and the results of profilometry in section 1 (Fig. 5(a,b)), the presence of moire contrast was determined when the (100) planes with $d_{(100)} = 0.21$ nm of two misoriented Ni crystallites of hexagonal structure (sp. gr. P63/mmc) are superimposed. The cubic structure of Ni (sp. gr. Fm-3m)



(a) (b) (c)

FIG. 4. TEM HR of the nanocrystalline component of the plasma-chemical composition obtained from the mechanical mixture VC–Ni: a – electron microscopic image with enlarged section 1; b – FFT transformation of section 1 and its interpretation; c – theoretical model of the V_2O_3 lattice (space group R-3c)

is illustrated in Fig. 5(a) (sections 2, 3), where, based on the results of FFT transformations (Fig. 5(c)), planes (111) and (200) with $d_{(111)} = 0.2$ nm and $d_{(200)} = 0.17$ nm intersecting at an angle of 57° are determined, which agrees well with the theoretical model of Ni crystal lattice shown in Fig. 5(d). In addition, it should be noted that cubic nickel covers the particle under study almost completely, as evidenced by the visualization of the family of (200) planes with $d_{(200)} = 0.17$ nm in Fig. 5(a) (section 3) and Fig. 5(d).

The electron microscopic studies of nanocrystalline particles VN–Ni showed (Fig. 6) that the refractory grain is represented by two cubic titanium oxynitrides $VN_{0.64}O_{0.08}$ (sp. gr. Fm-3m), $a = 0.4041$ nm and $VN_{0.19}O_{0.96}$ (sp. gr. Fm-3m), $a = 0.4106$ nm (Fig. 6(a,b)), see Table 1. According to the FFT data (Fig. 6(c)), $VN_{0.64}O_{0.08}$ is characterized by interplanar spacings $d_{(111)} = 0.238$ nm and $d_{(200)} = 0.207$ nm. The intersection angle of the presented planes, equal to 57°, is demonstrated in the enlarged image of the studied section of FFT transformation (Fig. 6(c)) and the theoretical model of cubic vanadium oxynitride $VN_{0.64}O_{0.08}$, which is crystallographically identical to the Ni model (Fig. 5(e)). The oxyntride $VN_{0.19}O_{0.96}$, in turn, is represented by the interplanar spacing $d_{(200)} = 2.099$ nm (Fig. 6(b)).

Based on the experimental results obtained in the work, it is possible to formulate the chemical mechanism of the organization of nanocrystalline particles VC–Ni and VN–Ni taking place in the quenching chamber of a plasma-chemical installation in a turbulent flow of nitrogen gas. This mechanism is based on the assumption that, in accordance with [24], the crystallization processes occurring in the quenching chamber of a plasma-chemical installation operating in a low-temperature plasma mode can be considered "quasi-equilibrium".

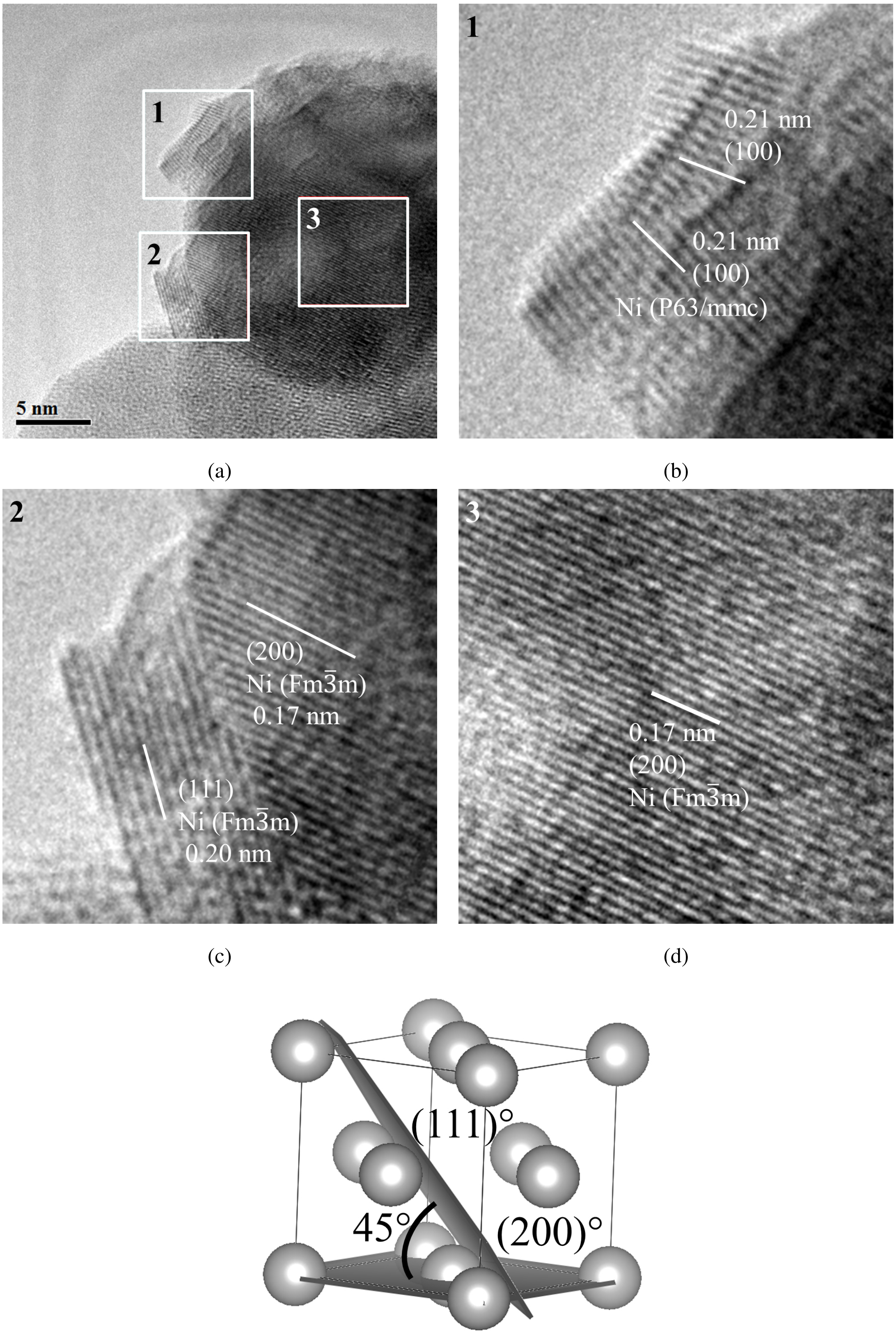
On this basis the quenching chamber, in which a turbulent flow of gaseous nitrogen is forcibly created, can be divided by temperature barriers. Table 3 shows the values of the boiling and melting temperatures of all phase components determined by X-ray diffraction [9, 10, 25, 26].

TABLE 3. Boiling and melting points of compounds included in the highly dispersed VC–Ni and VN–Ni compositions [9, 10, 25, 26]

Compound	T_{melt}, °C	T_{boil}, °C
$VC_{(cub.)}$	2800	3900
$VN_{(cub.)}$	2300	3100
Ni	1455	2900
C	3550	4827

The first temperature barrier, equal to 4000 °C, corresponds to the lower value of the temperature of existence of low-temperature plasma. Under these conditions, the evaporated carbon passes into a liquid state at 4827 °C and further crystallizes at 3550 °C, forming nuclei for subsequent crystallization of refractory vanadium compounds on them.

To verify the presence of free carbon, along with X-ray diffraction, the Raman scattering method was used to study the recondensed powders, Fig. 8. According to the results of the Raman studies, it can be said that carbon is present

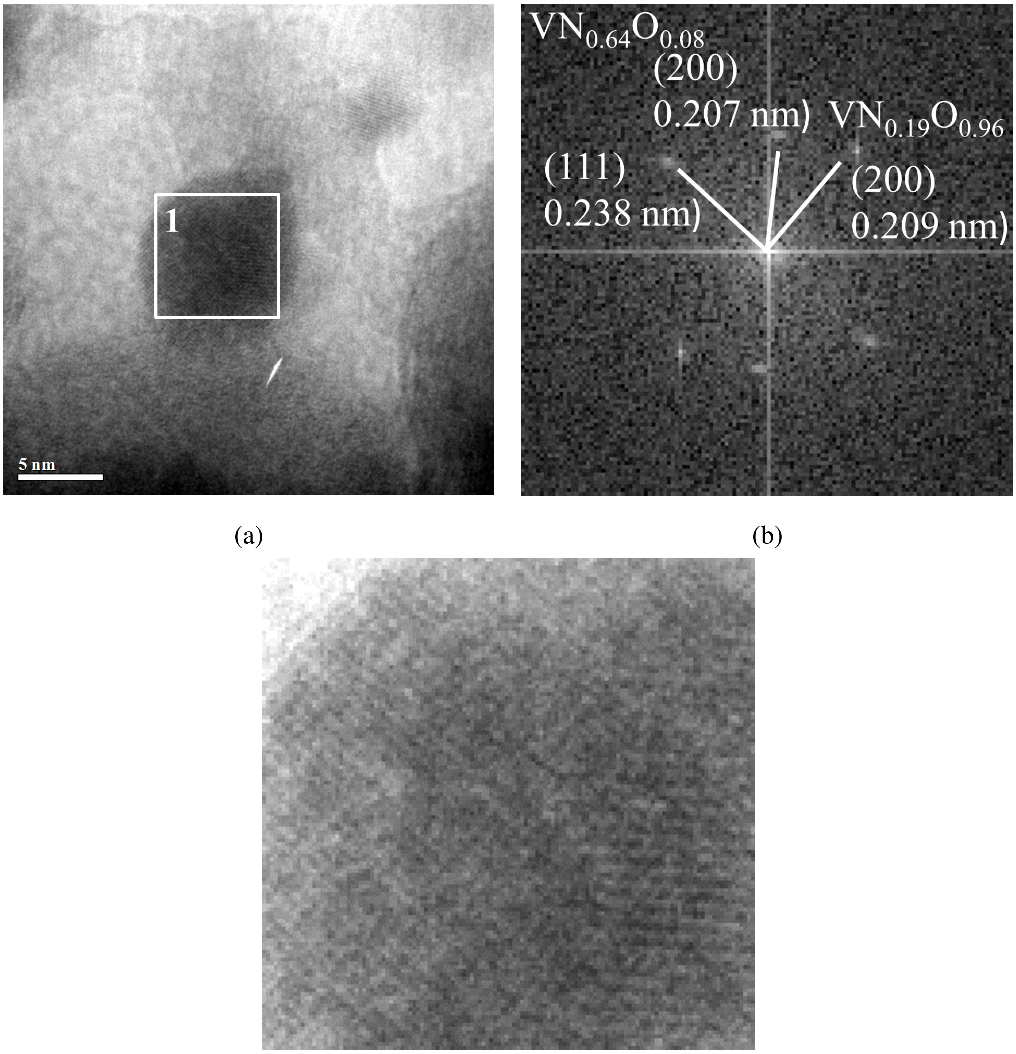


(a) (b)

(c) (d)

(e)

FIG. 5. HR TEM of surface layers of nickel in a nanocrystalline VC–Ni particle: a – electron microscopic image; b – enlarged image of section 1; c – enlarged image of section 2; d – enlarged image of section 3; e – theoretical model of Ni unit cell (sp. gr. Fm-3m) with planes (111) and (200)



(a) (b)

(c)

FIG. 6. HR TEM of a VN–Ni nanocrystalline particle with a core-shell structure: a – electron microscopic image with selected section 1; b – results of FFT transformation of section 1

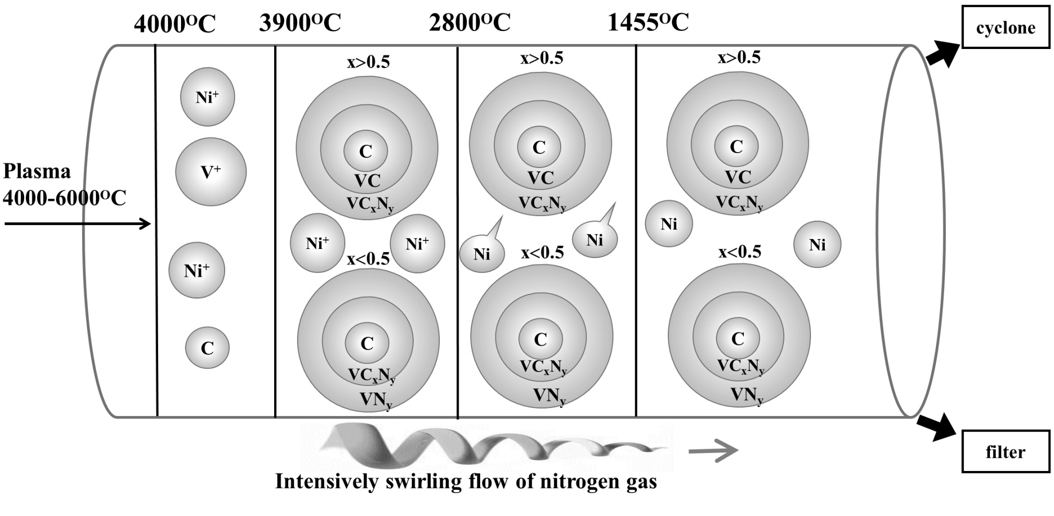


FIG. 7. Chemical mechanisms of organization of highly dispersed particles in the quenching chamber of a plasma-chemical installation, realized under conditions of low-temperature nitrogen plasma from mechanical mixtures of VC–Ni and VN–Ni

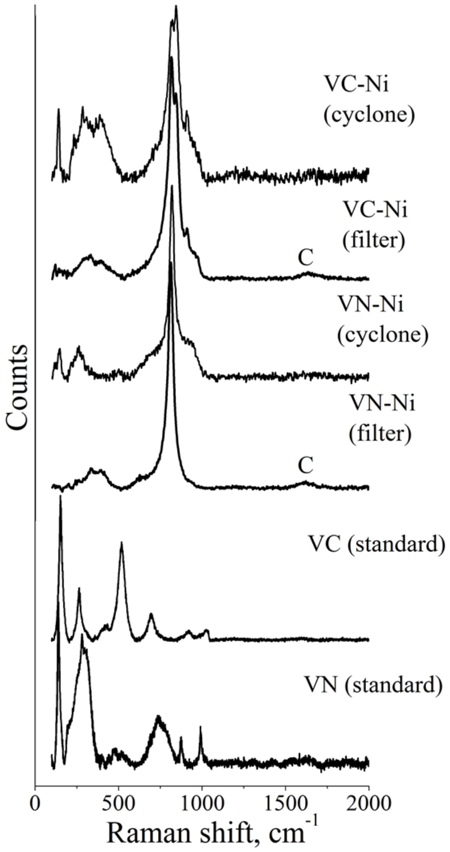


FIG. 8. Raman spectra of the obtained highly dispersed fractions of VC–Ni and VN–Ni

in nanocrystalline samples based on vanadium carbide (1634 cm^{-1}) and vanadium nitride from the filter (1619 cm^{-1}). Similar ultrafine fractions extracted from the cyclone do not exhibit any peaks of free carbon, which may indicate its presence in an amorphous state. The data of our studies of the chemical mechanisms in TiC–TiNi, TiC–Mo, TiC–Mo–Co can serve as an explanation for this effect [19, 26].

When passing the temperature barrier corresponding to the boiling point of vanadium carbide (3900 °C), the evaporated vanadium carbide VC condenses on the formed carbon nuclei. The resulting particles, due to the high crystallization temperature of VC (2800 °C), are formed in the form of refractory cores. The formation of oxycarbide and carbonitride phases is due to the presence of oxygen and nitrogen in the plasma-forming gas. The presence of oxygen in the system is due to the deactivation process.

The next stage of crystallization is the condensation of vanadium nitride VN, which boils at 3100 °C and crystallizes at 2300 °C. In this case, the formation of oxynitride phases occurs. The formation of vanadium oxides is due to the presence of oxygen in the system.

The final stage of crystallization is the condensation of metallic Ni, which boils at 2900 °C and crystallizes at 1455 °C. The formation of nickel particles occurs independently, which is confirmed by electron microscopic studies. The presence of vanadium in the nickel lattice was not detected.

Thus, the chemical mechanism of the organization of highly dispersed particles in the quenching chamber of a plasma-chemical installation, realized under conditions of low-temperature nitrogen plasma from mechanical mixtures of VC–Ni and VN–Ni, can be represented as follows (Fig. 9).

4. Conclusion

The work presents the results of studies of highly dispersed powder compositions based on vanadium carbide and vanadium nitride with metallic nickel, obtained under conditions of plasma-chemical synthesis in low-temperature nitrogen plasma.

X-ray studies have shown that the obtained plasma-chemical particles contain vanadium oxycarbides and oxynitrides, metallic nickel, and are also characterized by the presence of oxide phases of the V–O system. The presence of free carbon in the obtained compositions was confirmed by Raman spectroscopy.

Electron microscopic studies of nanocrystalline fractions of VC–Ni and VN–Ni powder compositions using high-resolution transmission electron microscopy visualized the structure of the obtained particles. Using the fast Fourier

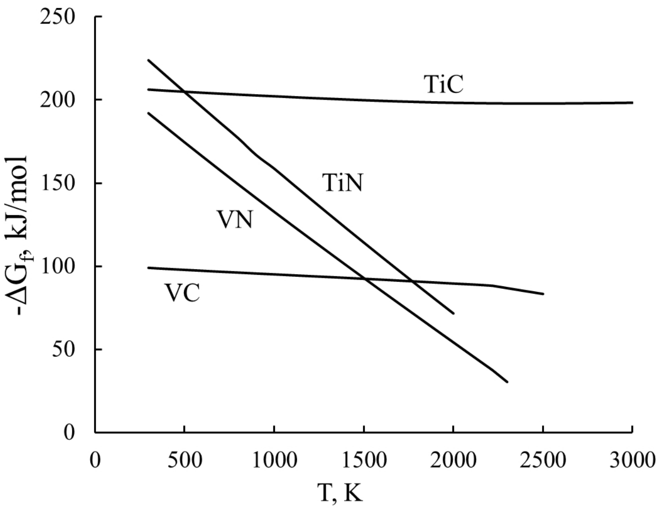


FIG. 9. Temperature dependences of $-\Delta G_f$ for VC, VN, TiC and TiN

transform, it was shown that the refractory components and metallic nickel form individual nanometer-scale particles that do not come into contact with each other.

A chemical mechanism of the organization of highly dispersed mechanical mixtures V–C–O–Ni and V–N–O–Ni under conditions of quenching processes in a turbulent flow of nitrogen gas proceeding at a speed of 10^5 °C/s has been formulated on the basis of the performed research.

References

[1] Ganji O., Sajjadi S.A., Yang Z.G., Mirjalili M., Najari M.R. On the formation and properties of chromium carbide and vanadium carbide coatings produced on W1 tool steel through thermal reactive diffusion (TRD). *Ceramics Int.*, 2020, **46** (16), P. 25320–25329.

[2] Zhukov M.F., Cherskiy I.N., Cherepanov A.N., Konovalov N.A., Saburov V.P., Pavlenko N.A., Galevskiy G.V., Andrianova O.A., Krushenko G.G. *Hardening of metallic polymeric and elastomer materials by ultrafine powders of plasma-chemical synthesis*. Novosibirsk: Nauka, 1999. 307 p.

[3] Carroll K. Core-shell nanoparticles: synthesis, design, and characterization. A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Richmond, Virginia: Virginia Commonwealth University, 2010. 209 p.

[4] Pang W., Li Y., De Luca L.T., Liang D., Qin Z., Liu X., Xu H., Fan X. Effect of metal nanopowders on the performance of solid rocket propellants: a review. *Nanomaterials*, 2021, **11** (10), 2749.

[5] Zaki Z.I., El-Sadek M.H., Ali H.H., Ahmed H. Synthesis of vanadium carbide by mechanical activation assisted carbothermic reduction. *Materials*, 2020, **13** (19), 4408.

[6] Chalmers B. *Principles of solidification*. John Wiley and Sons, Springer: New York, Dordrecht, Heidelberg, London, 1964. 319 p.

[7] Samsonov G.V., Upadhaya G.Sh., Neshpor V.S. *Physical Materials Science of Carbides*. Kyiv: Naukova Dumka, 1974. 455 p. (In Russian)

[8] Samsonov G.V. *Nitrides*. Kyiv: Naukova Dumka, 1969. 380 p. (In Russian)

[9] Krzhizhanovsky R.E., Shtern Z.Yu. *Thermophysical properties of non-metallic materials (carbides)*. Handbook. Leningrad: Energy, 1976. 120 p. (In Russian)

[10] Kosolapova T.Ya. *Handbook of high temperature compounds: properties, production, applications*. New York, Washington, Philadelphia, London: CRC Press, 1990. 958 p.

[11] Voitovich R.F. *Oxidation of carbides and nitrides*. Kyiv: Naukova Dumka, 1981. 192 p. (In Russian)

[12] Storozhenko P.A., Guseinov Sh.L., Malashin S.I. Nanodispersed Powders: Synthesis Methods and Practical Applications. *Nanotechnologies in Russia*, 2009, **4**, P. 262–274.

[13] Sadovnikov S.I., Gusev A.I. Effect of particle size and specific surface area on the determination of the density of nanocrystalline silver sulfide Ag_2S powders. *Physics of the Solid State*, 2018, **60**, P. 877–881.

[14] Shveikin G.P., Alyamovsky S.I., Zainulin Yu.G., Gusev A.I., Gubanov V.A., Kurmaev E.Z. *Compounds of variable composition and their solid solutions*. UC USSR Academy of Sciences, Sverdlovsk, 1984, 292 p. (In Russian)

[15] Schönberg N. The tungsten carbide and nicel arsenide structures. *Acta Metallica*, 1954, **2**, P. 427–432.

[16] Ermakov A.N., Luzhkova I.V., Avdeeva Yu.A., Murzakaev A.M., Zainulin Yu.G., Dobrinsky E.K. Formation of complex titanium-nickel nitride $Ti_{0.7}Ni_{0.3}N$ in the "core-shell" structure of TiN – Ni. *Int. J. of Refractory Metals and Hard Materials*, 2019, **84**, 104996.

[17] Avdeeva Yu.A., Luzhkova I.V., Ermakov A.N. Mechanism of formation of nanocrystalline particles with core-shell structure based on titanium oxynitrides with nickel in the process of plasma-chemical synthesis of TiNi in a low-temperature nitrogen plasma. *Nanosystems: Physics, Chemistry, Mathematics*, 2022, **13** (2), P. 212–219.

[18] Carbon. Access URL: https://prosto-o-slognom.ru/chimia/506_uglerod_C.html

[19] Avdeeva Yu.A., Luzhkova I.V., Ermakov A.N. Plasmachemical synthesis of TiC–Mo–Co nanoparticles with a core–shell structure in a low-temperature nitrogen plasma. *Russian Metallurgy*, 2022, **9**, P. 1019–1026.

[20] Morokhov I.D., Trusov L.I., Chizhik S.P. *Ultradisperse metallic media*. Moscow: Atomizdat, 1977, 264 p. (In Russian)

[21] Andrievskiy R.A. The synthesis and properties of nanocrystalline refractory compounds. *Russian Chemical Reviews*, 1994, **63** (5), P. 411–427.

[22] Gusev A.I. *Nanocrystalline materials: methods of production and properties*. Ekaterinburg: Publishing house of NIS UB RAS, 1998, 199 p. (In Russian)

[23] Polovov I.B., Volkovich V.A., Shipulin S.A., Maslov S.V., Khokhryakov A.A., Vasin B.D., Griffiths T.R., Thied R.C. Chemistry of vanadium chlorides in molten salts: An electronic absorption spectroscopy study. *J. of Molecular Liquids*, 2003, **103–104**, P. 387–394.

[24] Polak L. Elementary chemical processes and kinetics in a non-equilibrium and quasi-equilibrium plasma. *Pure and Applied Chemistry*, 1974, **39** (3), P. 307–342.

[25] Knunyants I.L. *Chemical Encyclopedia: in 5 volumes*. Vol. 3. Moscow: Soviet Encyclopedia, 1992. 639 p. (In Russian)

[26] Avdeeva Yu.A., Luzhkova I.V., Murzakaev A.M., Ermakov A.N. Plasma-chemical synthesis of highly dispersed core-shell structures from a mechanical mixture of titanium carbide and titanium nickelide. *Powder Metallurgy and Functional Coatings*, 2024, **18** (3), P. 5–15.

[27] Gusev A.I. *Non-stoichiometry, disorder, short-range and long-range order in a solid*. M.: FIZMATLIT, 2007. 856 p. (In Russian)

[28] Samokhin A.V., Polyakov S., Astashov A.G., Tsvetkov Yu.V. Simulation of the process of synthesis of nanopowders in a plasma reactor jet type. I. Statement of the problem and model validation. *Fizika i khimiya obrabotki materialov*, 2013, **6**, P. 40–46. (In Russian)

[29] Samokhin A.V., Polyakov S., Astashov A.G., Tsvetkov Yu.V. Simulation of the process of nanopowder synthesis in a jet-type plasma reactor. II. Nanoparticles formation. *Inorganic Materials: Applied Research*, 2014, **5** (3), P. 224–229.

[30] Shiryaeva L.S., Gorbuzova A.K., Galevsky G.V. Production and application of titanium carbide (assessment, trends, forecasts). *Scientific and Technical J. of the St. Petersburg State Polytechnic University*, 2014, **2** (195), P. 100–107. (In Russian)

Submitted 14 June 2024; revised 5 December 2024; accepted 6 October 2025

Information about the authors:

Yuliya A. Avdeeva – Institute of Solid State Chemistry of the Ural Branch of the Russian Academy of Sciences Pervomaiskaya Street, 91, Ekaterinburg, 620990, Russia; ORCID 0000-0002-1470-0476; y-avdeeva@list.ru

Irina V. Luzhkova – Institute of Solid State Chemistry of the Ural Branch of the Russian Academy of Sciences Pervomaiskaya Street, 91, Ekaterinburg, 620990, Russia; ORCID 0000-0001-9123-5371; key703@yandex.ru

Aidar M. Murzakaev – Institute of Electrophysics of the Ural Branch of the Russian Academy of Sciences, Amundsen Street, 106, Ekaterinburg, 620216, Russia; ORCID 0000-0003-4440-427X; aidar@iep.uran.ru

Alexey N. Ermakov – Institute of Solid State Chemistry of the Ural Branch of the Russian Academy of Sciences Pervomaiskaya Street, 91, Ekaterinburg, 620990, Russia; ORCID 0000-0002-2746-5292; ermakovihim@yandex.ru

Conflict of interest: the authors declare no conflict of interest.