Formation of ultra- and nanodispersed "core-shell" structures $Ti_{0.8}Mo_{0.2}C_{0.5}N_{0.5}$–Ni–Mo in the process of plasma-chemical synthesis of a mechanical mixture of titanium carbonitride with metallic nickel and molybdenum

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ABSTRACT Ultradisperse and nanocrystalline powder compositions were obtained in the process of plasma-chemical synthesis of a mechanical mixture of titanium carbonitride $TiC_{0.5}N_{0.5}$ with metallic nickel and molybdenum in a low-temperature nitrogen plasma (4000 – 6000 °C), taking into account recondensation in a turbulent flow of nitrogen gas. It was established by X-ray diffraction that their phase composition is characterized by the presence of cubic compounds in the form of titanium-molybdenum carbonitride $Ti_{0.8}Mo_{0.2}C_{0.5}N_{0.5}$, metallic Ni and Mo. High-resolution transmission electron microscopy was used to visualize a "core-shell" structure in the nanocrystalline fraction, which includes such phases as $Ti_{1-n}Mo_nC_xN_y$, Ni, NiO, TiO_2, $MoC_{0.5}N_{0.5}$.

The experimental data on measurements of the specific surface area by the BET method and the pycnomentric density made it possible to determine the calculated values of the average particle sizes which were 365 and 56 nm for the fractions from the cyclone and the filter, respectively. The average particle size of the nanocrystalline component of the fraction from the cyclone, according to the results of direct measurements, was 22 nm. Based on the obtained experimental results, a model for the formation of $Ti_{0.8}Mo_{0.2}C_{0.5}N_{0.5}$–Ni–Mo "core-shell" structures has been developed, which is implemented under the conditions of a turbulent flow of nitrogen gas formed in a quenching chamber of a plasma chemical plant.

KEYWORDS Titanium carbonitride, nickel, molybdenum, plasma-chemical synthesis, X-ray phase analysis, high-resolution transmission electron microscopy.

1. Introduction

The nanocrystalline state of substances is of considerable interest for both scientific experiments [1, 2] and practical application in various branches of technology [3–5].

It is known that single-phase nanocrystalline powders were initially obtained using various synthesis methods [6]. Such products required exceptional storage conditions due to their high chemical activity and, accordingly, pyrophoricity. In this context, methods for the passivation of highly dispersed materials providing long-term storage of especially nanocrystalline powder media under normal conditions were actively developed. Technologies of forced acidification, storage under a layer of liquid reagent, encapsulation of highly dispersed products with organic aerosols [7], etc. were used as passivation techniques.

At the same time, along with the development and improvement of methods for producing ultra- and nanodisperse materials, their separation and separation according to dispersed composition, density and specific surface area, experiments were performed to reduce the content of contaminants in highly dispersed systems. Such impurities, as a rule, were the materials of individual units of the installations in which synthesis was carried out (reactor walls, quenching chambers, cathodes, etc.) [8].

A more significant issue in the method of obtaining ultra- and nanodisperse materials is the formation of multiphase compositions, in which various phase components may be presented simultaneously, including those that cannot coexist within the same system or cannot be obtained using traditional ceramic technologies by solid-phase and liquid-phase synthesis. For the formation of multicomponent ultradisperse or nanocrystalline powder compositions, quite suitable are

certain methods for obtaining highly dispersed media aimed at atomic decomposition of the initial synthesis components under extreme exposure conditions. Such synthesis methods include gas-phase synthesis, plasma-chemical synthesis in low-temperature plasma, electric explosion of a conductor in a controlled gas atmosphere, and laser evaporation of a target [9].

The issues of the formation of microcrystalline solid solutions, complexly substituted in the metal sublattice, based on refractory titanium carbide-nitride compounds have been extensively studied and continue to be studied by scientists in many countries [10]. In particular, the introduction of IV – VIA metal elements into the metal sublattice promotes the formation of metal-ceramic compositions, provided that metal binders with participation of solid solutions of the $Ti_{1-n}Me_nC_xN_y$ type are introduced as binding phases [11]. For example, the introduction of metallic molybdenum into the TiC_xN_y – Ni system during liquid-phase sintering results in the formation of a metal-ceramic alloy, the refractory grains of which have a "core-shell" structure where titanium carbonitride TiC_xN_y acts as the core and $Ti_{1-n}Mo_nC_xN_y$ acts as the shell [12]. The intergranular spaces are filled with a Ni-Mo binder. The presence of titanium-molybdenum carbonitride $Ti_{1-n}Mo_nC_xN_y$ in the form of a shell allows using such metal-ceramic compositions as tool materials developed by a team of authors under the leadership of Academician G. P. Shveikin at the Institute of Chemistry of the USC of the USSR Academy of Sciences [13]. The resulting alloy has satisfactory physical and mechanical characteristics and is suitable for finishing steel during machining. Metal-ceramic compositions based on titanium carbonitride with nickel, alloyed with metallic vanadium [14] and zirconium [15], have similar properties.

The purpose of this study was to obtain an ultra- and nanodispersed charge powder – tungsten-free hard alloy, having a "core-shell" structure, where the refractory core is titanium-molybdenum carbonitride $Ti_{1-n}Mo_nC_xN_y$, coated with metal layers of Mo and Ni.

2. Methods

Plasma-chemical synthesis in a low-temperature ($4000 – 6000\ °C$) nitrogen plasma was chosen as the main method for the synthesis of highly dispersed materials [16]. The main technological characteristic of the plasma-chemical installation is its power, 25 kW (I = 90 A, U = 220 V). The productivity of the installation is 200 g/h. Process gas consumption: vortex chamber – 20 m³/h for hardening unit – 20 m³/h, 6 m³/h – for transportation of processed powders and separation in classifier 1 – vortex-type cyclone and classifier 2 – bag-type filter.

The composition of the mechanical mixture for plasma-chemical synthesis included 74.0 wt. % $TiC_{0.5}N_{0.5}$, 19.5 wt. % Ni, 6.5 wt. % Mo.

All the processed highly dispersed powders were subjected to encapsulation to reduce the chemical activity and, accordingly, pyrophoricity, which allows their long-term storage and safe use.

The resulting ultra- and nanodispersed powders based on titanium-molybdenum carbonitride $Ti_{1-n}Mo_nC_xN_y$, coated with layers of metallic Mo and Ni, were studied by X-ray diffraction methods (automatic X-ray diffractometer SHI-MADZU XRD-7000, CuK$_\alpha$ radiation, $2\theta = 5 – 100\ °$, shooting step 0.030) and high-resolution transmission electron microscopy (JEOL JEM 2100 LaB$_6$ cathode). The research results were processed using the ICDD and ICSD database files and WinXPOW and PowderCell 2.3 software. The results of electron microscopy studies were processed in the Digital Micrograph 7.0 software. The density of all the obtained ultra- and nanodispersed compositions was determined using a pycnometer (AccuPyc II 1340 V1.09).

Additionally, in accordance with BET methods, the specific surface area of all the obtained fractions was determined (specific surface area analyzer Gemini VII 2390 V1.03). Taken together, using formula (1) [17], based on density and specific surface data, estimated values of the average particle sizes were calculated, provided that their shape is spherical.

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

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

3. Results and discussion

Metal ceramics based on titanium carbonitrides TiC_xN_y with various metal binders [18–20], sintered from microcrystalline powder compositions according to mechanisms [21], have satisfactory mechanical characteristics. In this case, the use of plasma-chemical ultra- and nanodisperse powders, where all the phase components of tungsten-free hard alloys charge regulated by [22] are present within one particle with a "core-shell" structure, will improve the strength-plastic characteristics of instrumental metal ceramics.

Since the processes of evaporation and especially recondensation occurring in low-temperature nitrogen plasma in accordance with [23] can be characterized as "quasi-equilibrium", the physicochemical features of crystallization can be described under equilibrium thermodynamics conditions. In this work, it is proposed to introduce a metal, which is Mo, in the process of plasma-chemical synthesis in a low-temperature nitrogen plasma of a mechanical mixture $TiC_{0.5}N_{0.5}$–Mo–Ni, composed according to the formulation [22]. It is assumed that the introduction of molybdenum into the metallic sublattice of titanium occurs at the cooling stage in the quenching chamber at a rate of $10^5\ °$C/s, which can be expressed

by a decrease in the unit cell parameter of the TiC_xN_y carbonitride phase. It is also assumed that during the crystallization process, metallic Mo and Ni present in the initial charge are deposited in the form of individual layers.

The data of X-ray studies (Fig. 1) of the ultrafine fraction from classifier 1 – vortex-type cyclone (Table 1 No. 1) and the nanocrystalline fraction from classifier 2 – bag-type filter (Table 1 No. 2) show that both compositions have in their composition the phases of cubic (NaCl type) titanium carbonitride TiC_xN_y (sp. gr. Fm-3m), whose unit cell parameters differ significantly from the composition $TiC_{0.5}N_{0.5}$, as well as cubic Mo (sp. gr. Im-3m) and cubic Ni (sp. gr. Fm-3m). The nanocrystalline fraction from the bag-type filter, in addition to the above phases, contains nickel oxide NiO (sp. gr. Fm-3m). Besides, it should be noted that both fractions contain tetragonal titanium oxide TiO_2 (sp. gr. $P4_2$/mnm) in the form of stable rutile modification. The appearance of oxide phases in oxygen-free highly dispersed systems is due to forced acidification of recondensed powders in separation units (vortex-type cyclone and fabric filter) to reduce their pyrophoricity.
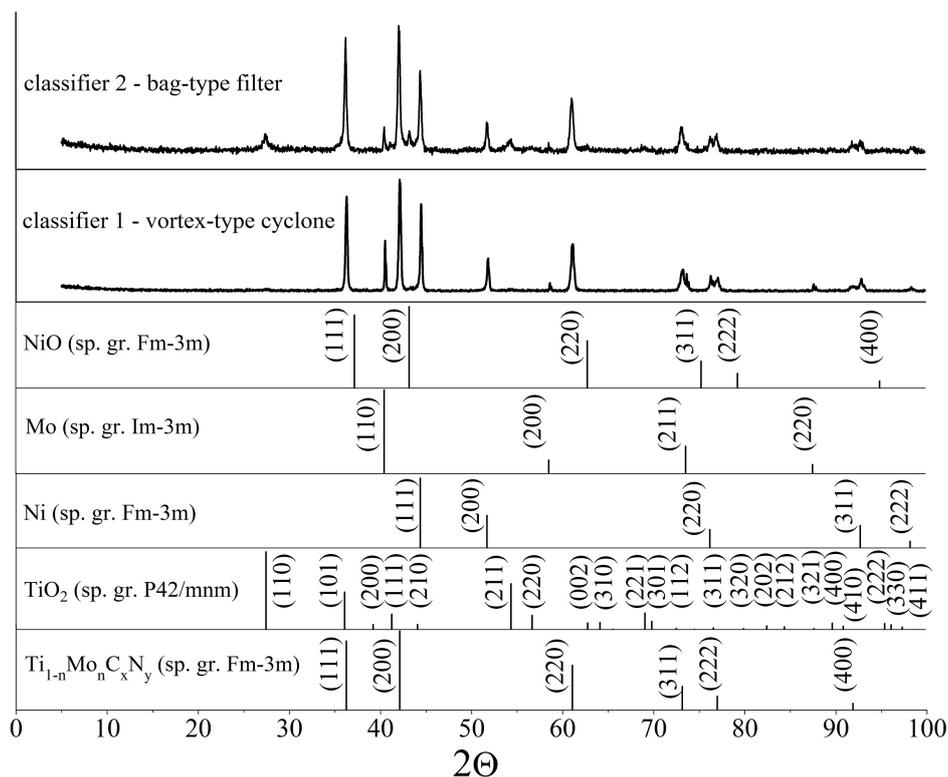

FIG. 1. Results of X-ray phase analysis of highly dispersed powders with a "core-shell" structure of the tungsten-free hard alloy charge based on titanium-molybdenum carbonitride $Ti_{1-n}Mo_nC_xN_y$ with the participation of Ni and Mo formed during plasma-chemical synthesis in a low-temperature nitrogen plasma

Electron microscopic studies (HRTEM) of the nanocrystalline component of a sample of the processed mechanical mixture $TiC_{0.5}N_{0.5} - Mo - Ni$ from classifier 2 – bag-type filter confirm the presence of a "core-shell" structure based on refractory cores of titanium-molybdenum carbonitride $Ti_{1-n}Mo_nC_xN_y$, coated with metal layers of cubic molybdenum and nickel (Fig. 2a).

Figure 2b illustrates the total particle size distribution histogram obtained on the basis of direct measurements in MEASURER software (developed at the Institute of Solid State Chemistry, Ural Branch, Russian Academy of Sciences), which shows that the average particle size is 22.0 ± 0.5 nm.

A detailed study of nanocrystalline particle is presented in Fig. 3. In particular, in section 1 (Fig. 3b) of the image, interplanar distances of 0.29 nm and 0.26 nm were determined based on the results of the fast Fourier transform, which belong to the (001) and (100) reflections of molybdenum carbonitride $TiC_{0.5}N_{0.5}$ of the hexagonal modification (sp. gr. R-6m2). In section 2 (Fig. 3c), the presence of a cubic NiO phase (sp. gr. Fm-3m) was detected, the unit cell parameter of which corresponded to 0.42 nm.

The presence of localized detected phases can be explained by the fact that in the process of plasma-chemical synthesis, along with the formation of titanium carbonitrides doped with molybdenum, the molybdenum carbonitride $MoC_{0.5}N_{0.5}$ is formed simultaneously, in good agreement with data [24]. The presence of NiO can be regulated by acidification of the surface of the nanopowder composition as a result of the slow flow of air into the chamber where the bag-type filter is located.

TABLE 1. Phase composition, density and average particle size (estimated by calculation) of ultrafine and nanocrystalline powders of Ti$_{1-n}$Mo$_n$C$_x$N$_y$ – Ni – Mo after plasma-chemical synthesis in a low-temperature nitrogen plasma

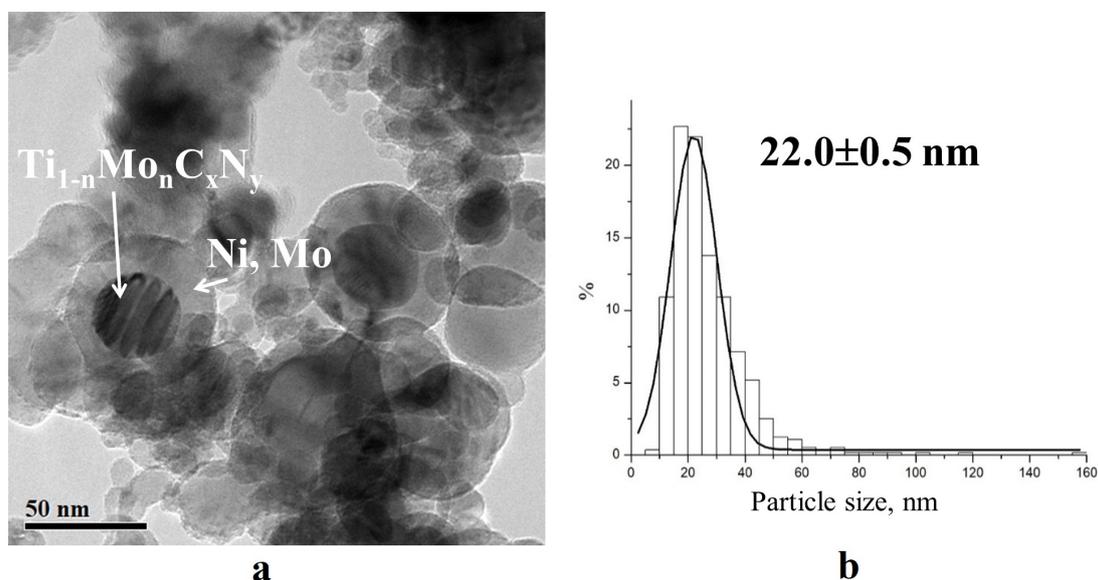| No.	Fraction	Phase composition (± 2 wt%), a, b, c (± 0.0001 Å)	S_{sp}, m^2/g	ρ, g/cm^3	d_{av}, μm
1	cyclone	Mo (Im-3m), (4 %), $a = 3.1482$; Ni (Fm-3m), (19 %), $a = 3.5276$; Ti$_{1-n}$Mo$_n$C$_x$N$_y$ (Fm-3m), (76. %), $a = 4.2883$; TiO$_2$ (P4$_2$/mnm) (1 %), $a = 4.5838$, $c = 2.9551$;	2.9	5.660	0.365
2	filter	Mo (Im-3m), (1 %), $a = 3.1474$; Ni (Fm-3m), (14 %), $a = 3.5272$; Ti$_{1-n}$Mo$_n$C$_x$N$_y$ (Fm-3m), (64 %), $a = 4.2873$; TiO$_2$ (P4$_2$/mnm)(15 %), $a = 4.5880$, $c = 2.9632$; NiO (Fm-3m), (6 %), $a = 4.1802$;	20.9	5.133	0.056

FIG. 2. HRTEM (a) of the nanocrystalline fraction of the processed mechanical mixture TiC$_{0.5}$N$_{0.5}$ – Mo – Ni from classifier 2 – bag-type filter and particle size distribution histogram (b)

Similarly, using the fast Fourier transform, interplanar distances of 0.25 nm and 0.34 nm corresponding to the (101) and (110) planes of TiO$_2$ (rutile) were determined on the surface of nanocrystalline particles of the Ti$_{1-n}$Mo$_n$C$_x$N$_y$ – Ni – Mo alloy charge, as shown in Fig. 4a,b.

Figure 5 shows the results of transmission electron microscopy of a single particle having a faceted shape (Fig. 5a). Based on the results of measurement of interplanar distances, it was established that the particle under study is covered with a layer of hexagonal modification C. The fast Fourier transform of the selected area (Fig. 5b,c) illustrates the presence of titanium-molybdenum carbonitride Ti$_{1-n}$Mo$_n$C$_x$N$_y$, which corresponds to an interplanar distance of 0.21 nm (200).

The results of electron diffraction studies of a polycrystalline sample (Fig. 6, Table 2) illustrate the presence of TiO$_2$ (sp. gr. P4$_2$/mnm) in the form of rutile, as well as cubic Ti$_{1-n}$Mo$_n$C$_x$N$_y$, NiO, Ni (sp. gr. Fm-3m).

Summarizing all the information received about the presence and localization of various phase components included in the composition of ultra- and nanodispersed compositions obtained as a result of recondensation of the mechanical mixture TiC$_{0.5}$N$_{0.5}$ – Mo – Ni, it is possible to formulate the chemical mechanism of the formation of nanocrystalline particles with a "core-shell" structure (Fig. 7). The mechanism should take into account the boiling and crystallization temperatures of all phase components detected by X-ray diffraction (Table 1). At the same time, the ΔG(T) dependences [24] should be taken into account to justify the absence of some compounds that could be formed in highly dispersed powder materials.
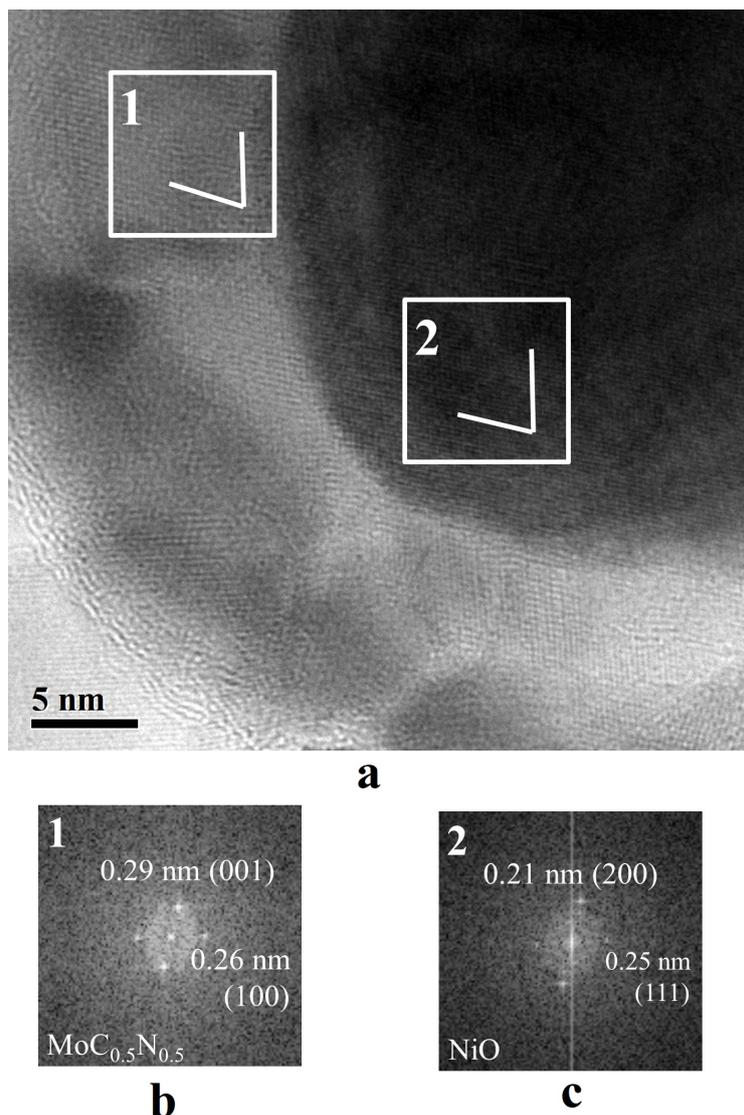
FIG. 3. Electron microscopic image of a nanocrystalline particle with a "core-shell" structure (a) of the $Ti_{1-n}Mo_nC_xN_y$ – Ni – Mo tungsten-free hard alloy charge, taking into account the fast Fourier transform processing of various image sections containing $MoC_{0.5}N_{0.5}$ (section 1) (b) and NiO (section 2) (c)

Modeling of the "core-shell" structure organization processes is based on the assumption that the space of the quenching chamber can be divided by temperature barriers along the axis of rotation of the tangential flow of nitrogen gas, provided technologically in the processes of recondensation of ultra- and nanodisperse particles in the quenching chamber of the plasmatron. A temperature of 4000 °C can be taken as an indicator of the first temperature barrier. At this temperature, the titanium carbide-nitride phases are in a gaseous state, because the crystallization temperature of titanium carbide TiC is 3300 °C, metallic Mo is in a similar state, and Ni is in the gaseous state. Upon reaching the second temperature barrier, characterized by the crystallization range of TiC and TiN, corresponding to 3300 – 2913 °C [25–27], crystallization of titanium carbonitride occurs by the "gas – solid" scheme, in accordance with works [28–31]. In the metal sublattice, a redistribution of positions between titanium and molybdenum ions takes place, taking into account the fact that its completeness is preserved according to reaction (2),

$$TiC_{0.5}N_{0.5} + Mo \rightarrow Ti_{1-n}Mo_nC_xN_{1-x} \qquad (2)$$
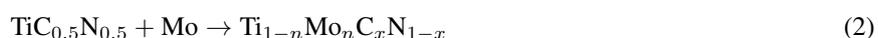
Gaseous nickel cannot react under these conditions due to its low affinity for carbon and nitrogen, which limits the formation of its carbide-nitride compounds compared to other metals located in the plasmatron chamber. The third temperature barrier corresponds to the crystallization temperature of Mo, 2623 °C. A little earlier, at a temperature of 2732 °C, nickel passes to a liquid state and can react with Mo, forming intermetallic compounds, which were detected by electron microscopic studies. Regarding the interaction of Mo with gas components, it should be noted that due to the redistribution of carbon and nitrogen over the complete non-metallic sublattice, only gaseous N_2, used as a coolant gas,
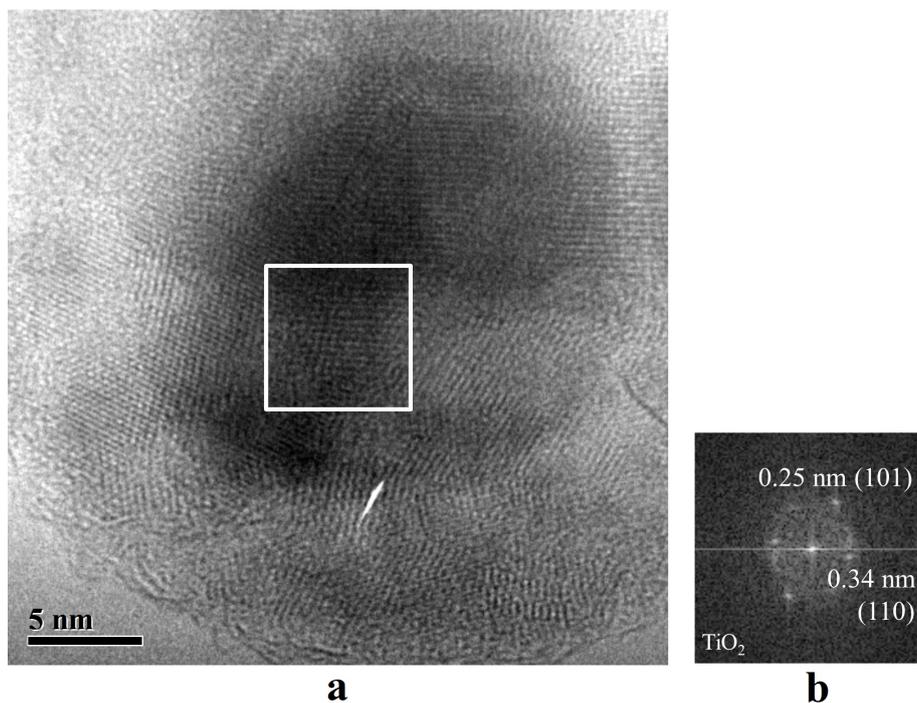
FIG. 4. Electron microscopic image of a nanocrystalline particle (a) of the Ti$_{1-n}$Mo$_n$C$_x$N$_y$ – Ni – Mo alloy charge and FFT transformation of a section of the particle (b)

TABLE 2. Results of decoding of the electron diffraction pattern (Fig. 6)

Ring number	d, nm	*hkl*, compound
1	0.32	(110) TiO$_2$ (P4$_2$/mnm)
2	0.24	(101) TiO$_2$ (P4$_2$/mnm) (111) Ti$_{1-n}$Mo$_n$C$_x$N$_y$ (Fm-3m)
3	0.21	(111) TiO$_2$ (P4$_2$/mnm (200) Ti$_{1-n}$Mo$_n$C$_x$N$_y$ (Fm-3m)
	0.20	(200) NiO (Fm-3m) (111) Ni (Fm-3m)
4	0.16	(220) Ti$_{1-n}$Mo$_n$C$_x$N$_y$ (Fm-3m) (211) TiO$_2$ (P4$_2$/mnm)
5	0.13	(311) Ti$_{1-n}$Mo$_n$C$_x$N$_y$ (Fm-3m) (301) TiO$_2$ (P4$_2$/mnm)

can participate in the reaction with liquid-phase Mo. However, in accordance with [24], the affinity of molybdenum for nitrogen is very low and, accordingly, molybdenum nitride cannot be formed under these conditions. Thus, Mo crystallizes in its individual form while maintaining a cubic lattice (sp. gr. Im-3m). The last temperature barrier is the crystallization temperature of liquid Ni, which corresponds to 1455 °C. Overcoming this temperature, metallic nickel crystallizes in the cubic modification (sp. gr. Fm-3m) completely covering the surface of ultrafine and nanocrystalline particles.

The presented chemical mechanism of the formation of nanocrystalline particles of the Ti$_{1-n}$Mo$_n$C$_x$N$_y$ – Ni – Mo tungsten-free hard alloy charge is in good agreement with the data of previously published works [32–36], describing the results of X-ray and electron microscopic studies, which were used as a basis to formulate the regularities of the organization of nanocrystalline particles with a "core-shell" structure of the composition TiC–Mo–Co, TiN–Mo–Co as a result of plasma-chemical synthesis in a low-temperature nitrogen plasma of mechanical mixtures containing titanium carbides and nitrides, metallic Mo and Co. The formation of nanocrystalline TiN-Ni particles with a "core-shell" structure
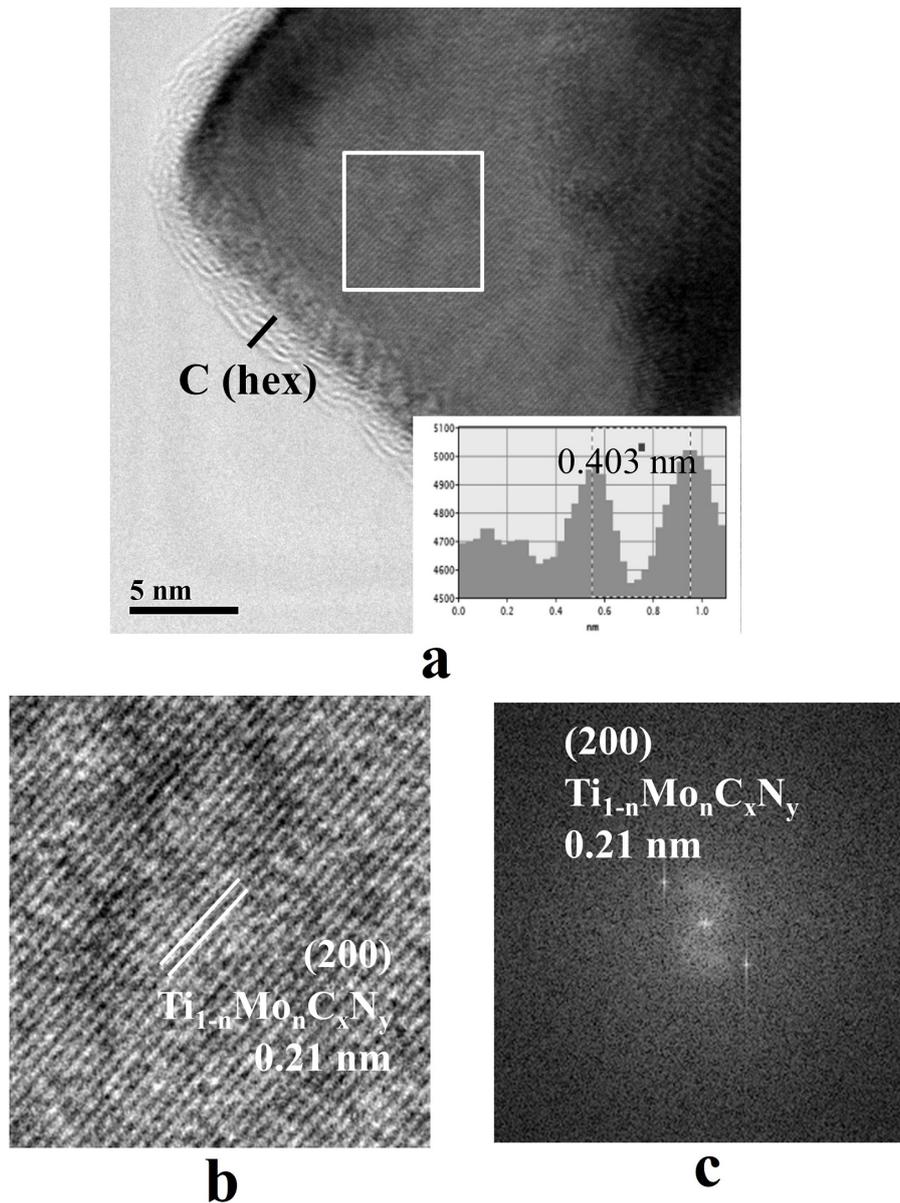
FIG. 5. Electron microscopic image (HRTEM) of (a) a nanocrystalline particle with a "core-shell" structure of the composition $Ti_{1-n}Mo_nC_xN_y$ – Ni – Mo coated with carbon, enlarged image (b) and its fast Fourier transform results (c)

as a result of plasma recondensation (4000 – 6000 °C) of TiNi titanium nickelide powder in a turbulent flow of nitrogen gas was considered in works [37, 38].

4. Conclusion

In the process of plasma-chemical synthesis in a low-temperature nitrogen plasma according to the plasma recondensation scheme, two highly dispersed fractions of the $Ti_{1-n}Mo_nC_xN_y$ – Ni – Mo tungsten-free hard alloy charge were obtained from a mechanical mixture of titanium carbonitride, nickel and molybdenum, which were certified by helium pycnometry and BET. The calculated values of the average particle sizes were 365 and 56 nm for the cyclone and filter fractions, respectively.

Based on the X-ray diffraction results, it was established that the plasma-chemical powder compositions contain cubic phases of titanium-molybdenum carbonitride $Ti_{1-n}Mo_nC_xN_y$, metallic Mo and Ni. TiO_2 and NiO formed as a result of forced acidification of the obtained highly dispersed powder compositions in the separation units of the plasma chemical plant are presented as additional phases.
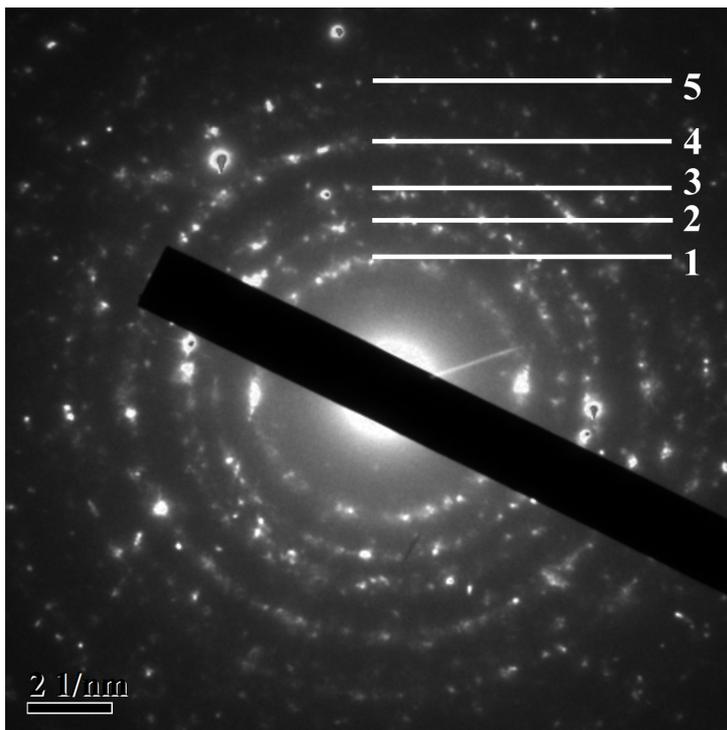
FIG. 6. Electron diffraction pattern of a polycrystalline sample of Ti$_{1-n}$Mo$_n$C$_x$N$_y$ – Ni – Mo
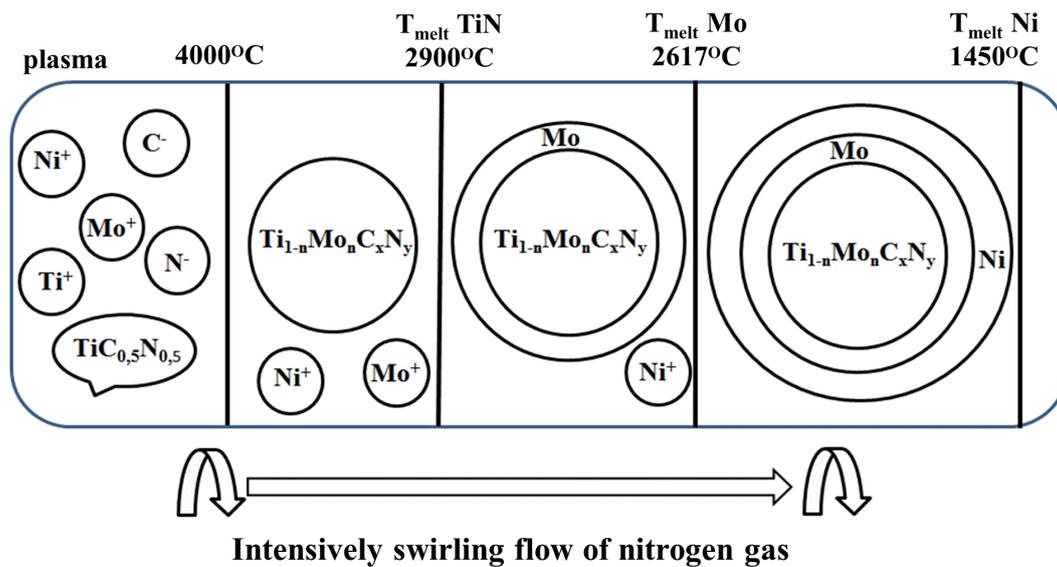

FIG. 7. Chemical mechanism of formation of nanocrystalline particles with a "core-shell" structure of the Ti$_{1-n}$Mo$_n$C$_x$N$_y$–Ni–Mo hard alloy charge, obtained by plasma-chemical synthesis in a low-temperature nitrogen plasma

The nanocrystalline component of the filter fraction was additionally investigated by high-resolution transmission electron microscopy; its average particle size according to direct measurements was 22 nm. The particles of the nanocrystalline component of the fraction from the filter represent a "core-shell" structure, in which the carbonitride $Ti_{1-n}Mo_nC_xN_y$ acts as the core, and metallic Mo and Ni act as individual surface layers.

Based on the obtained experimental results, a chemical mechanism for the organization of a "core-shell" structure under the conditions of a turbulent flow of nitrogen gas with a cooling rate of 10^5 °C/s has been formulated for nanocrystalline particles of the tungsten-free hard alloy charge containing titanium-molybdenum carbonitride $Ti_{1-n}Mo_nC_xN_y$ coated with metal layers of Mo and Co.

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