

Formation of titanium-cobalt nitride $\text{Ti}_{0.7}\text{Co}_{0.3}\text{N}$ under plasma-chemical synthesis conditions in a low-temperature nitrogen plasma

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Nanocompositions with “core-shell” structure are of interest in different areas of materials science and solid state chemistry, since, along with traditional refractory components in the form of carbides or nitrides and individual metals (Ni, Co), phases of mixed composition of the type $\text{Me}_{1-x}\text{Me}_2\text{N}$ (Me1 – a refractory element of IV-VIA subgroup, Me2 – Ni or Co) are formed during synthesis within one highly dispersed particle. It should be noted that such multicomponent phase components are metastable and cannot be obtained in an individual state. At the same time, phases of the $\text{Me}_{1-x}\text{Me}_2\text{N}$ type are formed in systems with participation of nitride compounds during extreme processing. In the present work, the technology of plasma-chemical synthesis with subsequent recondensation of gaseous nitrogen in a rotating cylinder was used.

The work is aimed at obtaining metastable complex-substituted titanium-cobalt nitride $\text{Ti}_{0.7}\text{Co}_{0.3}\text{N}$ in the framework of nano- and ultra-dispersed Ti(Mo)C–Co “core-shell” structures. All phase components of the claimed compositions were determined by X-ray diffraction. Additionally, Ti(Mo)C–Co nanoparticles were studied by high-resolution transmission electron microscopy and electron diffraction. It was determined that $\text{Ti}_{0.7}\text{Co}_{0.3}\text{N}$ has a strongly deformed stressed state, as evidenced by a single reflection (101) on the X-ray diffraction pattern. The paper also considers some aspects of crystal chemical design of $\text{Ti}_{0.7}\text{Co}_{0.3}\text{N}$ obtained in the course of structural and morphological certification of the Ti(Mo)C–Co nanocomposition.

Keywords: titanium-cobalt nitride, core-shell structure, plasma recondensation, low temperature plasma, X-ray phase analysis, high-resolution transmission electron microscopy.

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1. Introduction

Ultra- and nanodispersed materials have attracted much interest in terms of fundamental scientific research and technological applicability of the obtained powder media and samples compacted on their basis [1–5]. Of special interest are nanocrystalline materials obtained using techniques possessing a high productivity, relative simplicity and, what is important, environmental benignness and manufacturability of formation processes, including those in the form of “core-shell” structures [6–10].

One of the first methods for the formation of ultra- and nanodispersed products that meets the above requirements is plasma-chemical synthesis in a low-temperature gas plasma [11]. This technology features a high productivity (from 200 g/h), environmental friendliness and universal segregation procedures aimed at separating powder media in classifiers of the first type (vortex cyclones) and the second type (fabric bag filters). The number of collecting aggregates can be varied depending on the requirements for the final powder products, including distribution into fractions with a narrow particle size distribution. It should be noted that an important issue in the preparation of especially nanocrystalline media with the participation of various metals in the form of surface shells is reduction of the chemical activity and pyrophoricity of “core-shell” structures by different methods. For this purpose, capsulators are used in plasma-chemical installations. Capsulators are aerosol-type devices promoting the coating of active, highly-dispersed particles with vapors of organic compounds with an admixture of highly volatile technical liquids. The ultra- and nanodispersed particles processed in this way are suitable for long-term storage under normal conditions, which is important in the technological process.

In terms of physicochemical laws, plasma-chemical processes in a low-temperature nitrogen plasma are referred to “quasi-equilibrium” processes [12]. Quasi-equilibrium conditions promote the formation of stoichiometric compounds with individual crystallization of metals, regardless of their mutual chemical affinity, despite a substantially high crystallization rate in the quenching chamber of the plasmatron ($\sim 10^5$ °C/s). Under these conditions, ultra- and nanodispersed “core-shell” structures are formed in accordance with the laws set forth in the theory of heterogeneous nucleation by B. Chalmers [13]. In the framework of this theory, some aspects of interaction have been formed, including those between components having no mutual wettability with each other. In these cases, according to [13], during heterogeneous nucleation, crystallization of interlayer phases occurs, which include both elements

representing a refractory core and elements of metal shells. One of the first studies of the crystal-chemical features of complexly substituted hexagonal nitrides based on some elements of IV-VIA subgroups of the Periodic Table are Schonberg's works [14–16], where Ni and Co served as substitute elements in the metal sublattice. Later, nanocrystalline $\text{Ti}_{0.7}\text{Ni}_{0.3}\text{N}$ with a cubic modification was obtained and certified by X-ray diffraction and high-resolution transmission electron microscopy (HRTEM) [17]. In [18], plasma-chemical synthesis of titanium nickelide was carried out according to the plasma recondensation scheme in a low-temperature nitrogen plasma. In the fraction from the filter, a nanocrystalline composition TiN–Ni was recorded and certified, which included a similar nitride $\text{Ti}_{0.7}\text{Ni}_{0.3}\text{N}$. The HRTEM studies showed that the nanocrystalline composition was a “core-shell” structure. The refractory core corresponded to stoichiometric titanium nitride, while the metal shell was cubic modification Ni. Also, the hexagonal phase $\text{Ti}_{0.7}\text{Ni}_{0.3}\text{N}$ was found and certified [14] based on HRTEM studies with the use of profilometric measurements of interplanar distances and Fourier transform method. In particular, according to X-ray and electron microscopy data, titanium-nickel nitride was in a forcedly oriented state along the (101) direction, which is one of the main directions in the crystal structure of the corresponding space group P-6m2. In accordance with [19], the forcedly oriented state of titanium-nickel nitride can be explained by the effect of strong deformations in the process of extreme action during quenching of evaporated components in a rotating cylinder of gaseous nitrogen. Compaction of highly dispersed TiN–Ni powders was carried out under the conditions of liquid-phase vacuum sintering. These experiments showed that the interlayer phase component makes it possible to intensify the sintering processes due to the decomposition of $\text{Ti}_{0.7}\text{Ni}_{0.3}\text{N}$ into the Ti_2Ni intermetallic compound and gaseous nitrogen. The intermetallic phase in the intermediate layer melts at temperatures of 900 – 1100 °C, which intensifies the processes of melting of the metallic nickel shell with simultaneous solid-phase dissolution of the refractory TiN core [20]. Solid-phase dissolution processes proceeded until the solubility products of titanium nitride and metallic nickel were equalized in accordance with Humenik theory of liquid-phase interaction [21].

The aim of this work was to study the structural and morphological features of the $\text{Ti}_{0.7}\text{Co}_{0.3}\text{N}$ phase component, which is present in nanocrystalline Ti(Mo)C–Co compounds of various dispersed compositions depending on the stage of unloading.

2. Materials and methods

Plasma-chemical synthesis in a low-temperature nitrogen plasma taking into account crystallization by plasma recondensation was chosen as the main method for obtaining nanocrystalline materials. The synthesis is based on transferring a mixture of a plasma-forming gas with atomic components of precursor materials to a quenching chamber. The cooler gas in the quenching chamber is in the form of a rotating cylinder, then crystallization of the evaporated components of the initial charge occurs. The rotating cylinder of the coolant gas protects the final products of plasma-chemical synthesis from contamination by elements and compounds that make up the material of the quenching chamber walls. Industrial nitrogen was used as a plasma-forming gas, a cooling gas, and a transport gas. During crystallization, the powder substance is transported by the transport gas to the separating devices. The separating devices represent classifier 1 – a cyclone of vortex type, where the heaviest ultrafine particles settle, and classifier 2 – a bag-type fabric filter, where nanocrystalline fractions of recondensed products of plasma chemical synthesis are collected. The technological parameters of the plasma-chemical installation are shown in Table 1. In the course of the experiment, both single and double recondensations were carried out due to partial sampling of once-processed fractions and subsequent intensive mixing of the fractions from the cyclone and the filter in the dispenser. As the products of extreme synthesis were accumulated and cooled in the separators, the powder fractions were sent to the encapsulation unit. During encapsulation, all the obtained media were chemically treated with organic components to reduce the chemical activity and, accordingly, the pyrophoricity. The finely dispersed powders were encapsulated to provide their long-term storage under normal conditions.

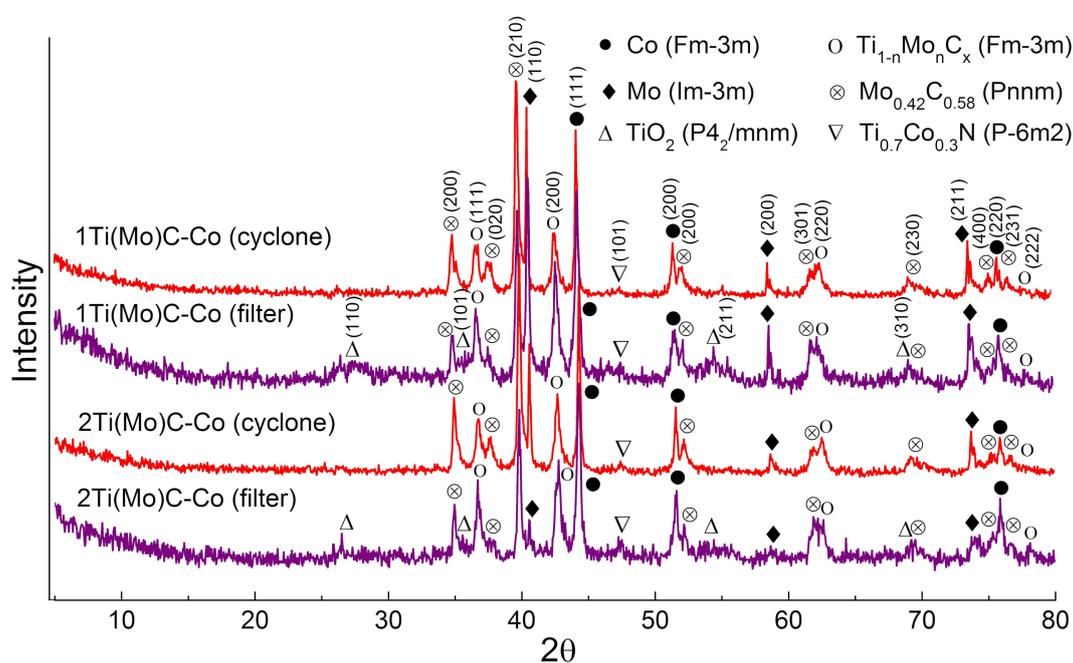
The recondensed ultrafine and nanopowder compositions were studied by X-ray phase analysis (automatic X-ray diffractometer SHIMADZU XRD 7000, $\text{CuK}\alpha$ cathode) and HRTEM (JEOL JED 2100). The obtained research results were processed using the modern software: WinXPOW, PowderCell 2.3 and SP ATOMS for processing X-ray data and constructing octahedral-tetrahedral coordination of the metastable complex nitride $\text{Ti}_{0.7}\text{Co}_{0.3}\text{N}$, as well as the Digital Micrograph 7.0 software package for interpreting atomic planes of various phase components entering into the composition of the nanocrystalline “core-shell” structures Ti(Mo)C–Co.

3. Results and discussion

The results of X-ray diffraction studies of nanocrystalline “core-shell” structures are presented in Fig. 1 and Table 2. Phase analysis and refinement of the unit cell parameters show that titanium-molybdenum carbide $\text{Ti}_{1-n}\text{Mo}_n\text{C}_x$

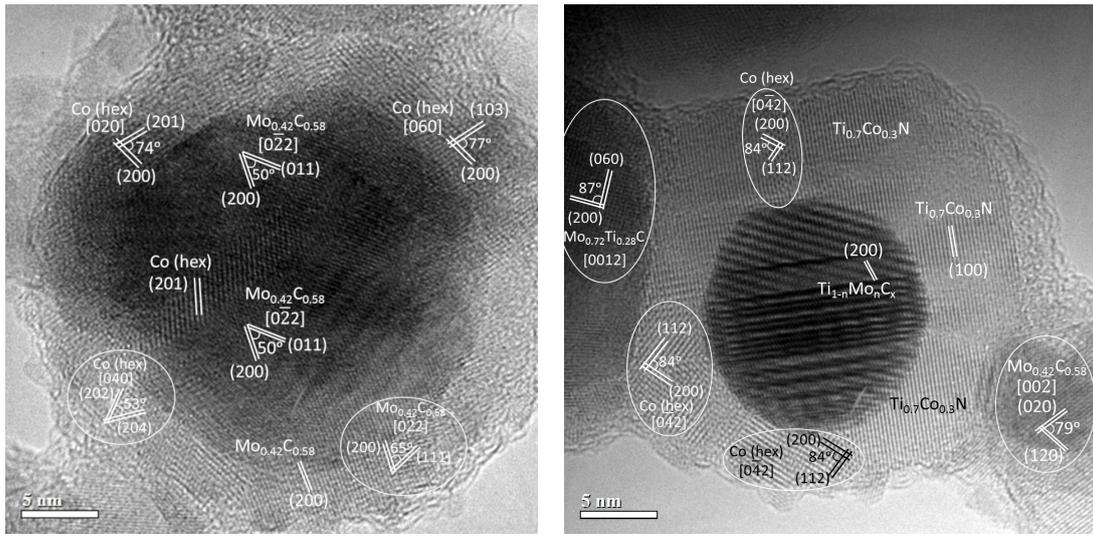
TABLE 1. Technical parameters of the plasma-chemical installation

Consumption of precursor mixture, g/h	200
Power of plasmatron, kW	25
Current strength, A	100 – 110
Voltage, V	200 – 220
Plasma flow velocity, m/s	60 – 100
Total nitrogen consumption in the plasma reactor, nm^3/h	25 – 30
Of the total nitrogen consumption for plasma formation, nm^3/h	6
Of the total nitrogen consumption for stabilization and quenching, nm^3/h	19 – 16

FIG. 1. X-ray diffraction patterns of $Ti(Mo)C-Co$ recondensed fractions in $5 - 80^\circ$

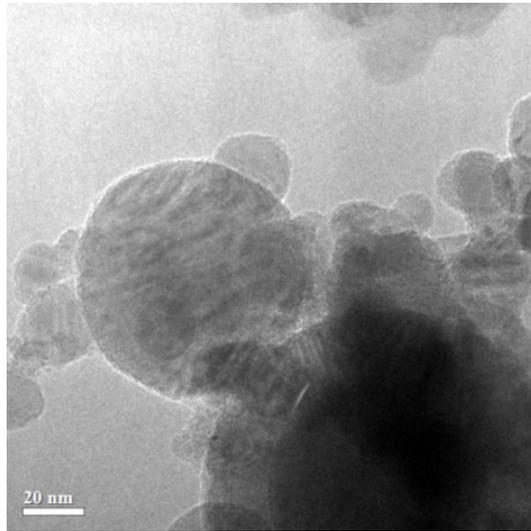
of the cubic modification, metallic Mo and its highly defective carbide $Mo_{0.42}C_{0.58}$ of the orthorhombic modification [22], as well as metallic Co of the cubic modification are formed in the process of plasma recondensation. The crystal chemical model of $Mo_{0.42}C_{0.58}$ is shown in Fig. 3a. A separate item is the phase formation of hexagonal (space group P-6m2) titanium-cobalt nitride $Ti_{0.7}Co_{0.3}N$, the standard crystallographic data of which are given in Table 2. The X-ray diffraction patterns of this phase have a single, considerably broadened reflection (101), which, in accordance with [19], is associated with a strongly deformed state caused by the extreme character of plasma recondensation. At the same time, the presence of a “core-shell” structure was proved using HRTEM by the example of singly recondensed particles of $Ti(Mo)C-Co$ fraction from the filter (Fig. 2a,b). Refractory titanium-molybdenum carbide $Ti_{1-n}Mo_nC_x$ acts as a core, and the shell, according to profilometric measurements and interpretation of the fast Fourier transform, contains metallic Mo, its highly defective carbide $Mo_{0.42}C_{0.58}$, hexagonal and cubic cobalt (Fig. 2b).

The presence of titanium-cobalt nitride $Ti_{0.7}Co_{0.3}N$, the crystal-chemical model of which is shown in Fig. 3b, in the form of a family of planes (101), (011), (100) in the framework of HRTEM was recorded by profilometry, fast Fourier transform, and electron diffraction methods (Fig. 2). In particular, the study of various image areas (Fig. 2b) reveals that titanium-cobalt nitride $Ti_{0.7}Co_{0.3}N$ almost completely covers the entire “core-shell” structure, including

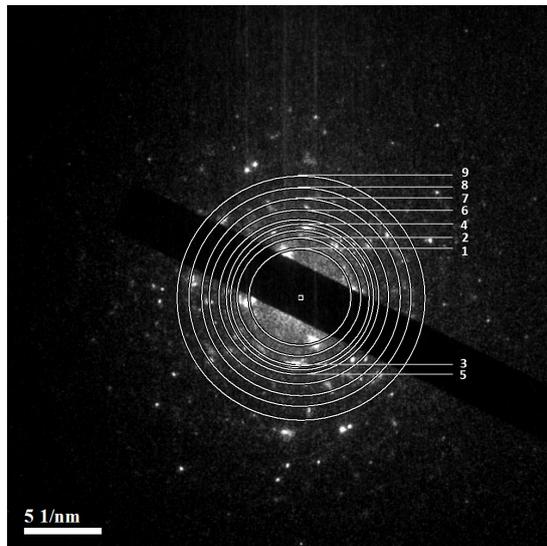


(a)

(b)



(c)



1. (011) $Ti_{0.7}Co_{0.3}N$
2. (100) $Ti_{0.7}Co_{0.3}N$
3. (111) $Mo_{0.42}C_{0.58}$
4. (200) $Ti_{1-n}Mo_nC_x$
5. (101) $Ti_{0.7}Co_{0.3}N$
6. (220) $Mo_{0.42}C_{0.58}$
7. (200) Mo
8. (311) $Mo_{0.42}C_{0.58}$
9. (220) Co

(d)

FIG. 2. HRTEM images of particles with “core-shell” structure (a,b), polycrystalline electron diffraction pattern (d) of the Ti(Mo)C–Co fraction from the filter (c)

TABLE 2. The results of X-ray phase analysis of recondensed fractions of Ti(Mo)C–Co

No.	Fraction	Phase composition, (± 2 wt. %), a , b , c , (± 0.001 Å)	ρ , g/cm ³	S_{sp} , m ² /g
1	1Ti(Mo)C–Co (cyclone)	Co (Fm-3m), (13 %), $a = 3.5514$; Ti _{1-n} Mo _n C _x (Fm-3m), (37 %), $a = 4.2459$; Mo (Im-3m), (6 %), $a = 3.1527$; Mo _{0.42} C _{0.58} (Pnnm), (44 %), $a = 5.1535$, $b = 4.8235$, $c = 2.9723$	5.3092	1.5243
2	1Ti(Mo)C–Co (filter)	Co (Fm-3m), (25 %), $a = 3.5494$; Ti _{1-n} Mo _n C _x (Fm-3m), (40 %), $a = 4.2408$; Mo (Im-3m), (2 %), $a = 3.1503$; Mo _{0.42} C _{0.58} (Pnnm), (22 %), $a = 5.1448$, $b = 4.8235$, $c = 2.9702$; TiO ₂ (P42/mnm), (11 %), $a = 4.748$, $c = 2.9349$	4.8778	8.8812
3	2Ti(Mo)C–Co (cyclone)	Co (Fm-3m), (17 %), $a = 3.5398$; Ti _{1-n} Mo _n C _x (Fm-3m), (33 %), $a = 4.2326$; Mo (Im-3m), (5 %), $a = 3.1422$; Mo _{0.42} C _{0.58} (Pnnm), (45 %), $a = 5.1302$, $b = 4.7952$, $c = 2.9638$	5.2619	1.8885
4	2Ti(Mo)C–Co (filter)	Co (Fm-3m), (26 %), $a = 3.5480$; Ti _{1-n} Mo _n C _x (Fm-3m), (45 %), $a = 4.2375$; Mo (Im-3m), (1 %), $a = 3.1474$; Mo _{0.42} C _{0.58} (Pnnm), (26 %), $a = 5.1413$, $b = 4.7960$, $c = 2.9719$; TiO ₂ (P42/mnm), (2 %), $a = 4.7635$, $c = 2.9219$	4.6690	10.9226

the refractory core of titanium-molybdenum carbide Ti_{1-n}Mo_nC_x. This illustration further confirms the layer-by-layer formation of phase components, including metastable compounds of highly defective molybdenum carbide and titanium-cobalt nitride.

Based on the results of experimental studies and previously published findings [18], it can be noted that the formation of metastable nitrides with a hexagonal crystal structure, which is complexly substituted in the metal sublattice, one of which is Ti_{0.7}Co_{0.3}N, takes place during high-speed crystallization with an excessive amount of cooling gas (N₂). In terms of colloidal-chemical regularities, in the process of crystallization of nanocrystalline “core-shell” TiN–Co structures, it is necessary to take into account the absence of mutual wettability effects between complete titanium nitride and metals of the iron subgroup under equilibrium conditions created by vacuum heating. At the same time, it is well known that titanium nitrides TiN_{1-x} in a highly defective state have prerequisites for certain conditions of wettability [23]. One of these formula compositions is TiN_{0.7}, which follows from the conditions of the presence of a wide homogeneity region in the Ti–N phase diagram.

The presence of complex titanium-cobalt nitride is also confirmed in the studies of ultra- and nanodispersed “core-shell” structures by DTA and TGA analysis in a protective argon atmosphere. In prior studies [20], a diffuse exothermic effect is observed at temperatures ranging from 500 – 550 °C, corresponding, according to X-ray phase analysis data, to the decomposition of Ti_{0.7}Ni_{0.3}N.

In the present work, the “core-shell” structures based on titanium carbides and nitrides with molybdenum and cobalt have been investigated by DTA and TGA methods under similar conditions under a protective argon atmosphere. Strongly diffuse exothermic effects were recorded, which correspond to the decomposition of the Ti_{0.7}Co_{0.3}N phase according to the equation:



The decomposition occurs at temperatures of 380 – 450 °C in all the obtained fractions of Ti(Mo)C–Co and TiN–Mo–Co, which is shown in Fig. 4.

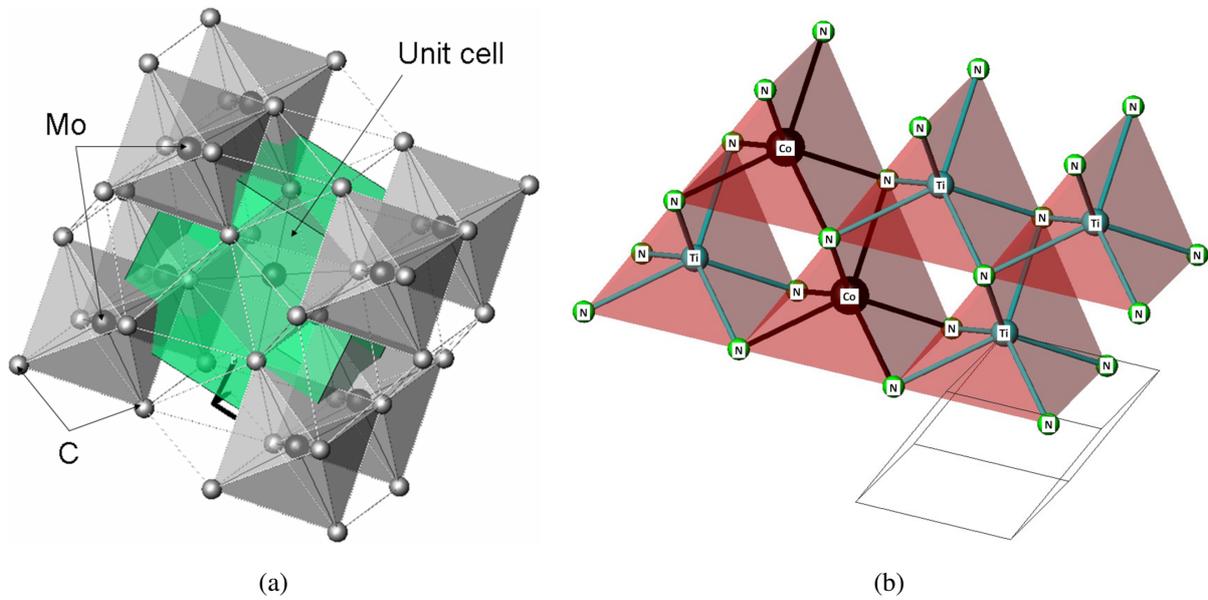


FIG. 3. Crystal-chemical model of orthorhombic $\text{Mo}_{0.42}\text{C}_{0.58}$ (a) and model of prismatic coordination of titanium-cobalt nitride $\text{Ti}_{0.7}\text{Co}_{0.3}\text{N}$ with reduced unit cell (b)

The complex nitride $\text{Mo}_{0.8}\text{Co}_{0.2}\text{N}_{0.9}$ obtained in [14] was not detected under the formation conditions for $\text{Ti}(\text{Mo})\text{C}-\text{Co}$ and $\text{TiN}-\text{Mo}-\text{Co}$ “core-shell” structures. The absence of compounds based on molybdenum nitride can be substantiated by the data of the $-\Delta G_f(T)$ dependence (Fig. 5) for similar nitrides TiN and MoN [24]. As seen from the graphs, the formation of compounds based on molybdenum nitride is virtually impossible due to the proximity of its values to 0.

At the end of the work, the results obtained can be compared with those described in prior literature. Table 3 shows the theoretical and experimental data for the similar metastable $\text{Ti}_{0.7}\text{Ni}_{0.3}\text{N}$ phase of various modifications [17]. Brief information on the complex titanium-cobalt nitride $\text{Ti}_{0.7}\text{Co}_{0.3}\text{N}$ obtained by plasma-chemical synthesis in a low-temperature nitrogen plasma with subsequent recondensation of gaseous nitrogen in a rotating cylinder is also presented.

4. Conclusion

In this work, nano- and ultradispersed $\text{Ti}(\text{Mo})\text{C}-\text{Co}$ compositions were obtained in the process of plasma recondensation in a low-temperature nitrogen plasma. In the course of HRTEM studies, the “core-shell” structure of $\text{Ti}(\text{Mo})\text{C}-\text{Co}$ nanoparticles was determined. In the composition of this structure, the $\text{Ti}_{0.7}\text{Co}_{0.3}\text{N}$ phase (space group P-6m2) of the hexagonal modification was determined with the use of X-ray diffraction and electron diffraction, which cannot be obtained in individual form. It was found that $\text{Ti}_{0.7}\text{Co}_{0.3}\text{N}$ is present as an interfacial layer between the refractory phase of cubic $\text{Ti}_{1-n}\text{Mo}_n\text{C}_x$ and metallic cobalt. The highly defective state of $\text{Ti}_{0.7}\text{Co}_{0.3}\text{N}$ is confirmed by the redistribution of line intensities and the presence of one reflection (101) in the X-ray diffraction patterns.

Nanocrystalline powders can be used as insoluble casting modifiers when pouring steels into molds coated with nanocrystalline powder. In this case, the dissolution of the cobalt shell with simultaneous preservation of the refractory core is allowed on contact of the molten metal with the nanoparticles. The core serves as a crystallization center, which can improve the strength and plastic characteristics of steel.

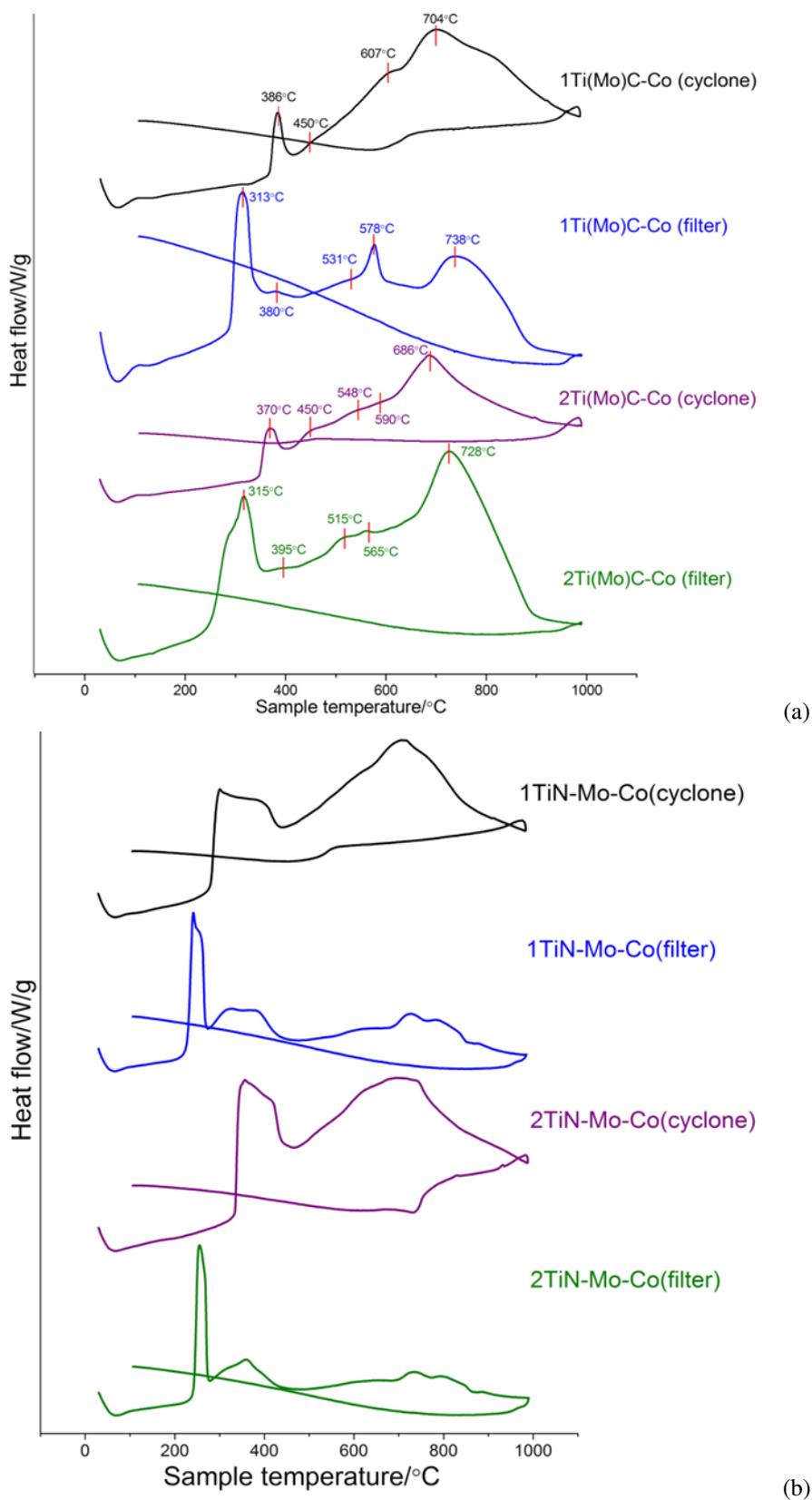


FIG. 4. DTA study of Ti(Mo)C-Co (a) and TiN-Mo-Co (b) fractions

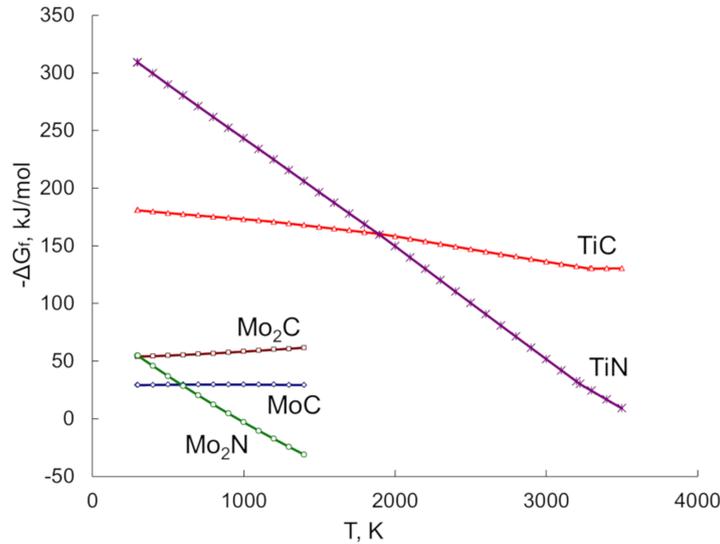


FIG. 5. Dependences $-\Delta G_f(T)$ for Mo_2N , MoC , Mo_2C , TiN and TiC compounds

TABLE 3. Information on the preparation and study of complex nitrides of the type $\text{Me}_1_{1-n}\text{Me}_2_n\text{N}_x$, where Me_1 – Ti, Mo, ... ; Me_2 – Ni, Co; $n \leq 1$

No.	Research performed	Literature source
1	For the first time, a number of complex nitrides $\text{Ti}_{0.7}\text{Co}_{0.3}\text{N}$, $\text{Ti}_{0.7}\text{Ni}_{0.3}\text{N}$, $\text{Mo}_{0.8}\text{Co}_{0.8}\text{N}_{0.9}$, $\text{Mo}_{0.8}\text{Ni}_{0.8}\text{N}_{0.9}$ were obtained and crystallographically certified.	[14]
2	Nanocrystalline $\text{Ti}_{0.7}\text{Ni}_{0.3}\text{N}$ with a cubic lattice was obtained by mechanochemical synthesis in an atmosphere of gaseous nitrogen. The nitride was certified by X-ray and transmission electron microscopy methods.	[17]
3	TiN-Ni powders were obtained by plasma-chemical synthesis in a low-temperature nitrogen plasma followed by recondensation in rotating nitrogen gas. Under conditions of liquid-phase vacuum sintering of nanocrystalline TiN-Ni powders, the role of $\text{Ti}_{0.7}\text{Ni}_{0.3}\text{N}$ was determined. According to additional DTA and TGA studies, it was found that $\text{Ti}_{0.7}\text{Ni}_{0.3}\text{N}$ decomposes into Ti_2Ni and gaseous N_2 . In turn, the decomposition reaction promotes a decrease in the sintering temperature of nanocrystalline samples by 300 °C.	[20]
4	High-resolution transmission electron microscopy of a TiN-Ni nanocrystalline sample obtained by plasma-chemical synthesis in a low-temperature nitrogen plasma was carried out. The $\text{Ti}_{0.7}\text{Ni}_{0.3}\text{N}$ phase is certified under the conditions of profilometric studies and fast Fourier transform.	[18]
5	X-ray and electron microscopic studies (HRTEM) under conditions of plasma recondensation of “core-shell” $\text{Ti}(\text{Mo})\text{C-Co}$ structures revealed the presence of titanium-cobalt nitride $\text{Ti}_{0.7}\text{Co}_{0.3}\text{N}$ in the nanocrystalline fraction from the filter.	The present work

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