

OBTAINING A COMPACT SUBGROUP OF VANADIUM NITRIDES USING THE APPROACH BY OXIDATIVE CONSTRUCTION OF THIN-WALLED CERAMICS (OCTC) AND INVESTIGATION OF ITS PROPERTIES

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Abstract

Oxidative construction of thin-walled ceramics (OCTC) is used to obtain compact niobium nitrides and vanadium nitrides with the given phase composition in the form of finished products. The change in the sample phase composition is studied at different temperature modes. The internal stresses calculated arising through the features of the material obtained by OCTC method.

Key words: ceramics, niobium nitride, vanadium nitride, compact nitrides, OCTC, resistive heating.

INTRODUCTION

Owing to significant advances in the technology of production of nitride materials over recent years, a real opportunity has appeared to use them as electronic components of instruments and units that would provide the service requirements following from the operating conditions of the equipment. Taking into account the physicochemical properties (refractoriness, high hardness, structural stability at high temperatures, high thermal conductivity and thermal stability, high chemical resistance), nitride ceramics seems to be a very promising material for modern electrical engineering as well as for the chemical industry [1, 2]. The following methods of nitride production have received the widest acceptance: annealing of metaloxides with coal in nitrogen or ammonia current, nitriding of metal or metal hydride powders with nitrogen or ammonia, exchange of decomposition of metalchlorides or oxychlorides under ammonia atmosphere, and isolation from a gas phase (growing method) [3]. All these methods give nitride powders which then are sintered to give final products. Several stages of the process and restricted design of the resulting items posed the problem of preparation of compact nitrides in the form of products by a one-step method. For the first time, titanium subgroup compact nitrides were prepared using the OCTC approach in [4]; the methodological bases for the production of monolithic nitrides were also developed. The goal of present work is to obtain vanadium subgroup nitrides via a one-step method using the OCTC approach and study their phase composition.

EXPERIMENTAL

A specially designed unit was used, for the production of monolithic niobium nitride. That allows one to conduct the synthesis at a constant nitrogen temperature and pressure. The samples were subjected to resistive heating. A detailed description of the unit for nitride synthesis and the principles of its operation are presented in [4]. The experiments were carried out with gaseous nitrogen of analytical grade (GOST (State Standard) 9293_74) purified from traces of oxygen via passing through a furnace filled with zirconium, heated to 450°C. The samples subjected to nitridation were obtained from niobium wire of NB_1 trademark with the diameter of 0.86 mm and length of 270 mm. The wire was washed in a UZDN-A ultrasonic bath and then vacuumed annealed at the temperature of $0.6 T_{mp}$ for 2 h. The samples were prepared in the form of helices with the internal diameter of 8 mm. To provide a constant electrical contact, the legs of a preform were fixed in copper current leads at a depth of 8 mm. The preform was heated to 700°C for 2–3 s and then gradually heated to the synthesis temperature at the rate of 50°C/min. The experiments were performed in a temperature range from 1300°C to 2300°C with the step of 100°C. At 1600, 1800, 2100, and 2300°C, nitrides of stoichiometric compositions were obtained. For different modes, the holding time ranged from 20 to 1800 min at the nitrogen pressure of 152 kPa. As a result, niobium nitride samples differing in the phase composition and physical properties were obtained. (international bank of powder diffraction standards, 2003). Scanning electron microscopy (SEM) of transversal facets and elemental energy dispersive analysis were performed with a CarlZeissNVISION 40 device. The microhardnesses of the resulting nitride samples were measured with a DURAMIN II microhardness tester. XRD nalysis of powders prepared from the fragments of compact nitrides was carried out using an XRD_6000 Shimadzu diffractometer in the range of 2θ angles from 20° to 80° in CuK α radiation at $\lambda = 1.5417$ E. XRD

patterns were identified using a JCPDS data bank. The superconducting properties of the material were analyzed on the Quantumdesignppms device.

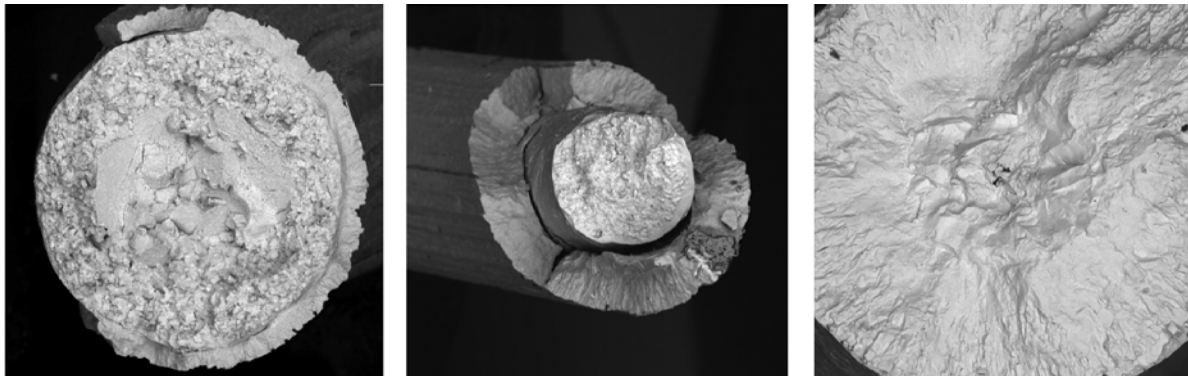


Fig. 1. SEM micrographs of niobium nitride facets at different synthesis temperatures and holding times: (a) 1600°C, 60 min; (b) 1600°C, 120 min; (c) 1800°C, 120 min.

RESULTS AND DISCUSSION

In performing the nitridation in a temperature range from 1300 to 2100°C and for a holding time of over 20 min, for all the samples, an insignificant increase in the initial preform diameter (by 2–4%) at complete retention of the starting geometry and its surface relief (traces of die broaching) was observed. For the samples syntheses at 1600°C for a period of less than 180 min, the sample nitridation did not proceed to a full extent. Figures 1a and 1b show the micrographs of the samples with the synthesis time of 60 and 120 min respectively.

The external nitride layer consists of Nb₄N₃ and Nb₂N phases. The layer thickness increases due to exposure. The internal layer represents a solid solution of nitrogen in niobium. The mechanical impact led to lamination of the nitride layer. The increase of the synthesis temperature up to 1800°C and holding time to 120 min affords the formation of a mixture of Nb₄N₃ and Nb₂N nitrides along the whole sample section; therefore, it is impossible to reveal a boundary between the nitride layer and metallic matrix on this facet (Fig. 1c). The

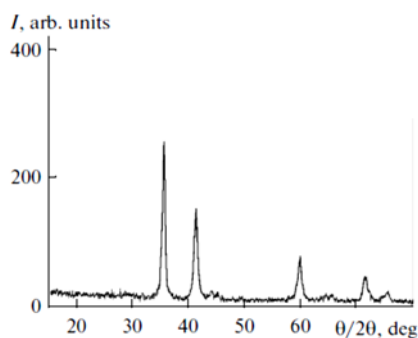


Fig. 2. XRD pattern for NbN; all the peaks correspond to NbN phase.

Nb₄N₃ phase, which is confirmed by XRD patterns presented in Fig. 4. On the basis of an array of experimental data, it can be concluded that the saturation of metallic niobium with nitrogen proceeds according to the following scheme: Nb → solid solution → Nb₂N → Nb₄N₃. The phase transitions taking place during the nitridation reaction lead to the continuous change in the total resistivity of the sample. We took the absence of changes in the volt-ampere characteristics of a power plant for 20 min as a parameter of termination of the synthesis.

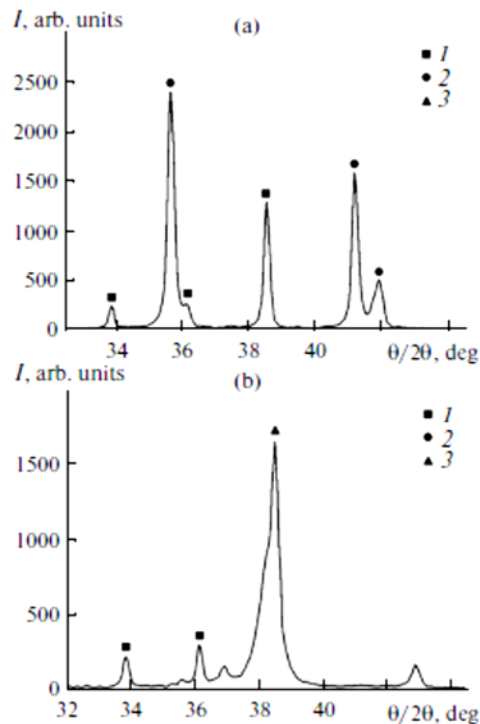


Fig. 3. XRD patterns for the (a) external nitride layer and (b) internal modified matrix: (1) Nb₂N, (2) Nb₄N₃, (3) Nb.

The published data [5] that describes the methods of nitrides production other than oxidative construction show that the samples with short synthesis times manifest nonuniformity of mechanical properties, which can be connected with the energy nonuniformity of the metal surface (appearance of defects on the surface). Nitrogen adsorbed faster on the active sites of the metal surface; at the same regions, there arise nuclei and then isles of nitride phases [5]. The nitrogen diffusion along the grain boundaries proceeds much more rapidly than that over the grain volume, which leads to the formation of a solid solution of nitrogen in niobium and the Nb₂N phase, affording, in turn, the nonuniformity of mechanical properties. The derived experimental data on mechanical nonuniformity are in a good agreement with the published data which note that at short nitridation times (10–20 min) the process is unstable and hardly reproducible [6].

The samples with short holding times are characterized by nonuniformity of the composition across the section, which is supported by the data of energy dispersive elemental analysis and microhardness values. The measurements were performed in three regions of a microsection: at ~50 μm from the sample surface, at a quarter of the section (the region at a distance of ~215 μm), and in the geometrical center. The results of energy dispersive analysis are presented in Table 1.

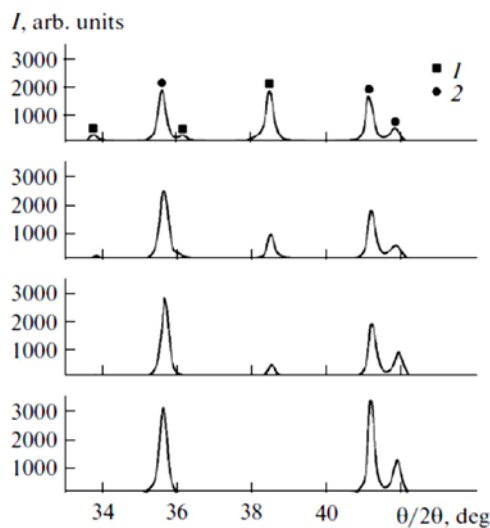


Fig. 4. XRD patterns for the samples of niobium nitridebearing the (1) Nb₂N and (2) Nb₄N₃ phases at the synthesis temperature of 1800°C and different holding times: (a) 60 min; (b) 120 min; (c) 180 min, (d) 300 min.

Table 1. Results of energy dispersive analysis

Sample no./holding time	Spectrum	N, wt %	Nb, wt %	Total
1/60 min	1	7.52	92.48	100.00
	2	6.83	93.17	100.00
	3	3.09	96.91	100.00
2/120 min	1	10.65	89.35	100.00
	2	6.90	93.10	100.00
	3	5.53	94.47	100.00
3/180 min	1	11.97	88.03	100
	2	9.75	90.25	100
	3	6.65	93.35	100
4/300 min	1	11.60	88.40	100
	2	12.20	87.80	100
	3	11.43	88.57	100

During the experiment optimal temperature and time parameters of the stoichiometric synthesis of vanadium nitride VN were established. Residual stress typical for vanadium nitride obtained by oxidative design affect its

Residual stresses can significantly change the properties of materials influencing the behavior during processing, use or even during storage[7]. Residual stresses can amplify or attenuate the working voltage, algebraically add

up to them. Typically, tensile residual stresses are most dangerous because they lead to destruction when added to the tensile stresses from external loads, although these loads may be insignificant[8].

To measure the residual stresses arising from vanadium nitride obtained using the procedure of oxidative design, original x-ray technique was used. The original X-ray method was used to measure the residual stresses occurring in vanadium nitride obtained using the method of oxidative construction. This method is [9] in compared with the standard “sin2Ψ” method allows to avoid errors in the measurement of the lattice parameters associated with the solid solution concentration nonuniformity of embedded nitrogen. In the measurement of residual stresses by “sin2Ψ” method the amount of deformation of the lattice is calculated from the following relationship

$$\varepsilon_{\psi} = \left(\frac{1+\nu}{E}\right)_{hkl} \sigma_{oct.} \sin^2 \psi + 2\left(\frac{\nu}{E}\right)_{hkl} \sigma_{oct.} \quad (1)$$

Where ν - Poisson's ratio, E - Young modulus, Ψ - the angle between the normal to the specimen surface and the normal to the plane of reflection (the diffraction vector) It was shown [4] that for estimation of residual stresses lattice parameters of grains where different reflection plane parallel to the plane of the sample can be analyzed (where $\Psi=0$). In this case, equation (1) becomes

$$\varepsilon_{\psi=0} = \frac{\Delta a_{\sigma}}{a_0} = 2\left(\frac{\nu}{E}\right)_{hkl} \sigma_{oct.} \quad (2)$$

Thus, the amount of deformation of the lattice, for any system of crystallographic planes is determined by the residual stresses and the anisotropy of the elastic moduli.

For a cubic lattice, the value of $(\nu/E)_{hkl}$ is defined by the relation:

$$(\nu/E)_{hkl} = S_{11} + J\Gamma \quad (3)$$

where $J = S_{11} - S_{12} - 0,5S_{44}$ - anisotropy parameter,

$$\Gamma = (h^2k^2 + h^2l^2 + k^2l^2)/(h^2 + k^2 + l^2)^2 -$$

orientation factor. after substituting 2 in 3 and $S_{11} + J\Gamma =$

$$\Delta a_{\sigma} = \frac{K_{hkl} \text{ initialization}}{2a_0 \sigma_{ocm.} K_{hkl}} \quad (4)$$

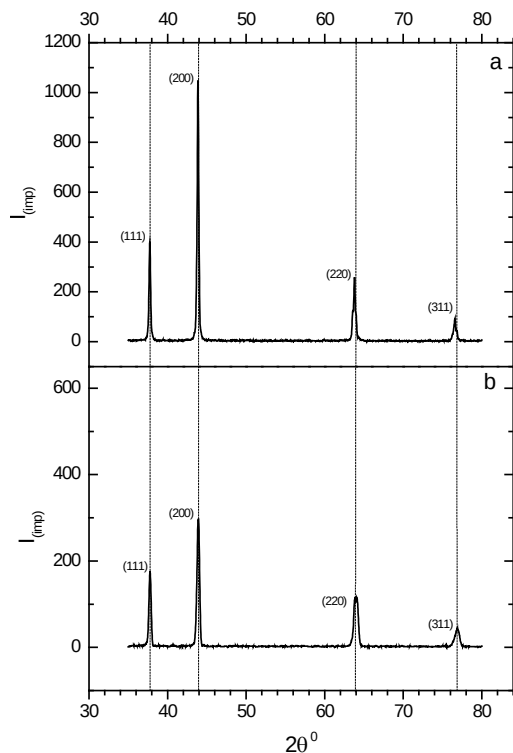


Fig.5 XRD synthesized compact vanadium nitride powder (a), the plate (b)

residual stress:

$$\sigma_{ocm.} = \frac{a_{h_1 k_1 l_1} - a_{h_2 k_2 l_2}}{2(a_{h_2 k_2 l_2} K_{h_1 k_1 l_1} - a_{h_1 k_1 l_1} K_{h_2 k_2 l_2})} \quad (5)$$

To evaluate the significance of residual stresses in the samples of vanadium nitride obtained by the oxidative construction method, we used published data of the Young's modulus and Poisson's ratio [10] and the lattice parameters calculated from X-ray diffraction using method described above. The residual stress was $\sigma = +3,4$ GPa i.e. the tensile stress.

Vanadium nitride VN has a wide homogeneity of nitrogen 16,4-21,6% wt. [6], it can also affect the lattice period. Fig. 6 shows the variation of the lattice constant on the nitrogen content.

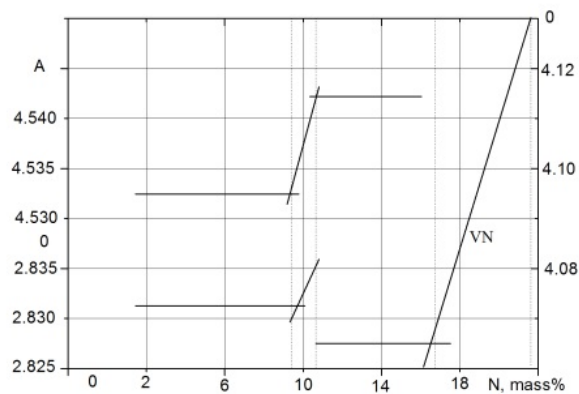


Fig. 6 shows the variation of the lattice constant on the nitrogen content wt%. [11]

V3N is homogeneous phase in the range of 9.3 - 10.5 wt.% of nitrogen. Alloys up to 9.3% of nitrogen are two-phase α -solid solution phase and V3N. From 16.4 - 21.6 wt.% of nitrogen homogeneous phase VN. The calculated lattice parameters of the diffraction patterns for vanadium nitride powder are in good agreement with the literature ($a = 4,123\text{-}4,126 \text{ \AA}$) [11]. The SEM images (Fig. 7) at low magnifications (a, b) clearly shows that the resulting crystallites have a columnar shape and properly oriented with respect to the plane of the surface of the base metal

blank Small-crystallite structure that takes the form of a columnar solid VN, which is typical for the cast materials, is observed near the surface of the sample. The area of pores oriented parallel to the surface is observed in the geometric center of the sample. The formation of those pores is probably connected with the features of the material obtaining using the approach of oxidative construction. At greater magnifications (Fig. 7 c, d) a small number of pores occurs in the crystallite formations. This may be related to the presence of the chemical contaminants in the raw metal, whose absence leads to the formation of a dense vanadium nitride. A comparative analysis of experimental and literature data presented in the table 2. It may be noted that the values of micro-hardness of vanadium nitride obtained using the approach of oxidative construction is not worse than the value for the material obtained by the classic method. The difference in density values may be related with the presence of a certain amount of closed pores in the material which may occur due to the features of that material obtaining. Relation between temperature and resistance that shown on picture 8 clearly shows the superconducting transition at 6 K

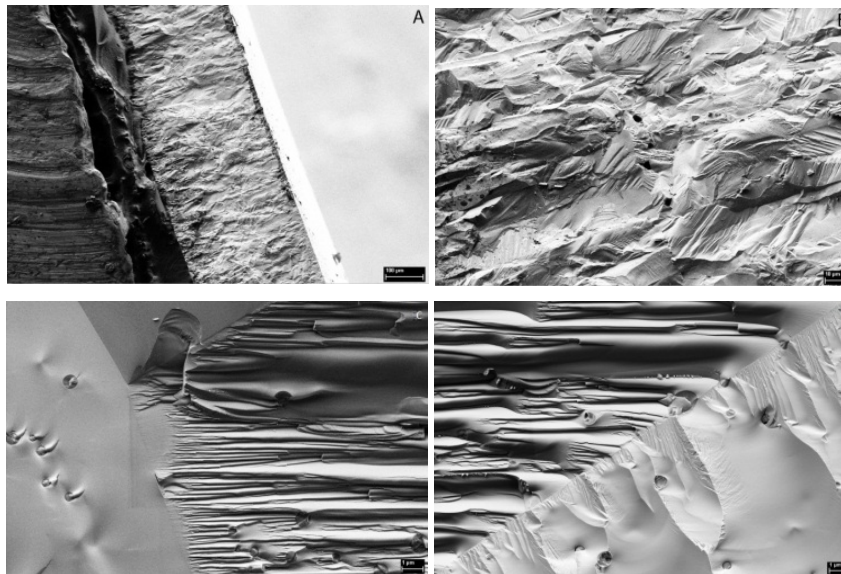


Fig.7 SEM images cleaved with increasing vanadium nitride 250x (a), 1500x (b), 10000x (c) and 15000x (d)

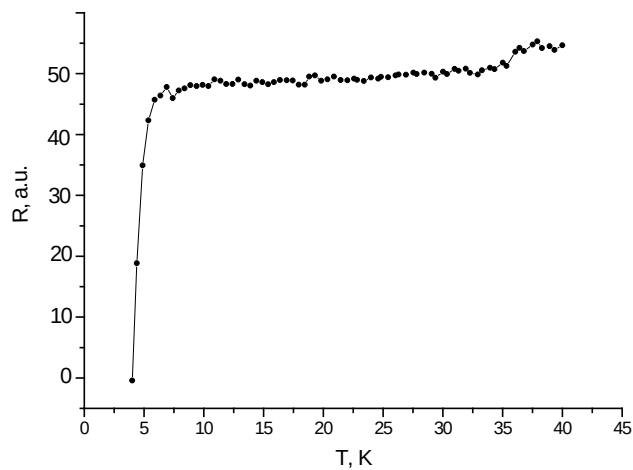


Fig.8 Temperature dependence of the electrical resistivity of vanadium nitride

Table 2. Physical characteristics are as vanadium nitride

Characteristics	Experimental data	Literature data
Microhardness HV	1222±143 (press down – 200 g, time 15 sec.) 1470±170 (press down – 100g, time 15sec.)	1520±115 (press down 50g)[7]
Pycnometric density	$\rho=5,968\text{g/cm}^3$	$\rho=6,040\text{g/cm}^3$ [7]

CONCLUSIONS

We show the possibility of using of the oxidative design approach for compact vanadium nitride and niobium nitride obtaining as a finished product. We conduct a set of physical studies of this material (micro-hardness, density, superconductivity) and comparison with the properties of material obtained by classical methods. The optimal parameters of the synthesis of ceramic samples.

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