Self-propagating high-temperature synthesis of cubic niobium nitride under high pressures of nitrogen

A.V. Linde [a,b], V.V. Grachev [a], R.-M. Marin-Ayral [b,*]

[a] Institute of Structural Macrokinetics and Materials Science (ISMAN), Russian Academy of Sciences, Chernogolovka, Moscow 142432, Russia
[b] Institut Charles Gerhardt Montpellier (ICGM), PMOF-UM2-CNRS, Pl. E. Bataillon, 34095 Montpellier Cedex 5, France

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ABSTRACT

Cubic niobium nitrides δ-NbN$_x$ with different $x = 0.87$–1.015 were prepared by the self-propagating high-temperature synthesis (SHS) under nitrogen pressures of $P(N_2) = 48$–230 MPa.

Nitrogen composition x as a function of $P(N_2)$ was determined in weight gain experiments and compared with that determined by chemical (Kjeldahl) analysis. For powders with different x, the super-conducting transition temperature T_c was measured as a function of lattice parameter a. The T_c values were found to grow linearly with increasing a. A maximum value of $T_c = 15.0$ K for cubic niobium nitride corresponded to a maximum value of $a = 4.3901$ Å.

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1. Introduction

Among the nitrides of transition metals, cubic niobium nitride δ-NbN$_x$ has the highest superconducting transition temperature $T_c = 17.3$ K [1–3]. Critical temperature depends on crystal imperfection, in particular on the concentration of vacancies in the metal and nonmetal sublattices which can be characterized by the value of lattice parameter a [4]. The less the imperfection of both sublattices (the lower the concentration of metal and nonmetal vacancies) the higher the value of a. In other words, the higher the a value the higher the T_c value. In turn a depend on the nitrogen/niobium atomic ratio x, upon variation in which, concentrations of nitrogen and niobium vacancies vary. The a behaviour as a function of x has not yet been completely explained and a matter to which x exactly corresponds a maximum value of a is still actual. It is believed that a maximal a corresponds to a stoichiometric nitride with $x = 1.00$ [4–6]. On the other hand, it corresponds to a slightly substoichiometric nitride with $x \approx 0.98$ [7–9]. The establishment of such a maximum is important for clarification of the properties of δ-NbN$_x$.

For obtaining the stoichiometric composition, high pressures of nitrogen are required. There are several publications which describe the synthesis of δ-NbN$_x$ powders via SHS without dilution of an initial sample with final nitride product. Some data for the pressure range 330–1260 MPa was given in [10]. For cylindrical samples of 10 mm in diameter a maximal composition $x = 0.98$ (under 1260 MPa) was obtained, whereas for samples of 15 mm in diameter both stoichiometric ($x = 1$ under 330 MPa) and overly stoichiometric ($x = 1.01$–1.02 under 450–805 MPa) compositions were obtained. In [11] δ-NbN$_x$ with maximal $x \approx 0.93$ (under 1000 MPa) was obtained over the pressure range 70–1000 MPa. These two pioneering studies [10,11] were performed under very high nitrogen pressures, whereas later investigations were performed under much lower pressures. The researches [12–17] report about the synthesis of δ-NbN$_x$ powders via SHS in nitrogen gas, a maximum pressure value being less than 10 MPa and incomplete conversion being observed (x was less than 0.976). Buscaglia et al. [3] obtained cubic niobium nitride with $x = 1.02$ (under 70 MPa). However, in this work it was synthesized in thermal explosion mode rather than in SHS-mode. High extent of nitriding in thermal explosion mode was attained both due to higher initial temperature of the synthesis and due to higher initial nitrogen pressure than in [12–17].

Superconducting cubic niobium nitride powders can be also prepared by high-temperature reactive diffusion [5,18], plasmo-chemical synthesis [19] and by the direct nitridation of amorphous Nb$_2$O$_5$ powders in ammonia atmosphere at high temperatures [20,21].

The synthesis of δ-NbN$_x$ with different x via SHS occurs according to the reaction:

$$Nb(s) + N_2(g) \rightarrow NbN_x(s)$$
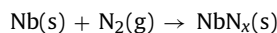
* Corresponding author. Tel.: +33 0 467143355; fax: +33 0 467144290.
 E-mail address: rose-marie.ayral@univ-montp2.fr (R.-M. Marin-Ayral).

Producing of substoichiometric δ-NbN$_x$ seems to be not so complicated since it can be obtained under relatively low nitrogen pressures. The synthesis of nitride with x above the unity (1.01 or 1.02) via classical SHS without dilution of starting sample with final nitride product seems to be much more complicated as very high pressures are required [10,11]. However upon combustion synthesis, heat loss from the sample into environment is another essential parameter which also influences conversion extent and decrease of heat loss seems to increase x. Firstly, because more heat will be kept in the reaction zone and, secondly, because the combustion product will cool down slower that will give an additional time for the nitridation reaction at high temperature (the so-called "after-burning stage" [22,23]). Thus the aim of this work was to obtain an overly stoichiometric δ-NbN$_x$ via classical SHS without dilution of starting sample with final nitride product under lower nitrogen pressures than in [10,11]. For that, a combination of high nitrogen pressures with heat insulation of the samples was used.

The $a(x)$ and $T_c(a)$ functions for substoichiometric ($x < 1$) and overly stoichiometric ($x > 1$) compositions will be also investigated.

2. Experimental

All experiments were carried out in a high pressure SHS-reactor under nitrogen pressures of $P(N_2) = 48$–230 MPa. To prepare a starting sample (15 mm in diameter, 40 mm in height, porosity of 51–53%), Nb powder (average particle size 43 μm, 99.8 wt.%) was put into a cylindrical container of gas permeable filter paper. For decreasing heat loss the sample was put into a graphite container filled with BN powder as it is shown in Fig. 1. Loose BN powder with high porosity of 80–85% practically did not prevent nitrogen infiltration to the sample from the reactor volume. The ignition of Nb samples was accomplished by a tungsten coil heated with a current and by several grams of Ti powder. The combustion temperature was measured with two WRe 5/WRe 20 thermocouples of 0.2 mm in diameter (with an occurrence of ±50 °C) inserted in the core of a sample and at 25 mm of each other. The combustion velocity was determined using obtained thermograms with an occurrence of ±0.5 mm/s. The pressure was measured with a piezosensor.
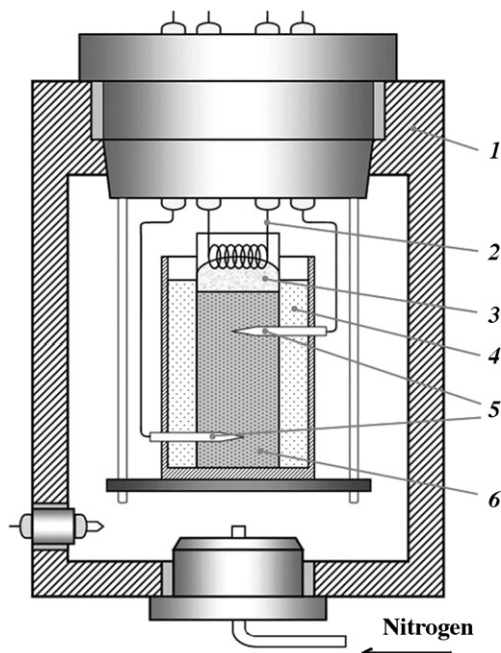
The readings from the thermocouples and the piezosensor were recorded with a computer data acquisition system.

The SHS product was characterized by XRD. The diffraction patterns were taken with a Phillips Expert diffractometer (Cu K$_{\alpha1}$ radiation, $2\theta = 15$–125°, angle pitch 0.017°, acquisition time 1024 s). The lattice parameter of synthesized cubic niobium nitrides a was determined using the Celref software with an initial value of 4.3927 Å for cell refinement and with an accuracy of ±0.0005 Å.

Overall nitrogen composition of the product was determined in weight gain experiments. Weight gain was measured with an accuracy of ±0.01 g that upon conversion into coefficient x in δ-NbN$_x$ gives also $\Delta x = 0.01$. Nitrogen distribution in a cross-section of burned sample was determined by chemical analysis (using Kjeldahl method [24]) of two probes from the central and middle layers (see Section 3.2). Whole the middle layer was not analyzed. The powder which was closer to the surface of a sample was taken (but not including a powder from the surface layer). The accuracy of determination of nitrogen content by Kjeldahl method was ±1.5 wt.% that upon conversion into coefficient x in δ-NbN$_x$ gives $\Delta x \approx 0.01$ (similar to weight gain experiments).

Micrographs were taken with a Jeol JXCA-733 X-ray microanalyzer with Oxford Instruments' INCA system for energy dispersive microanalysis (EDS), which was used for determination of the combustion product composition with an accuracy of $\Delta x = 0.01$. Magnetic susceptibility was measured with a Quantum Design MPMS-XL SQUID magnetometer working in the temperature range 1.8–300 K and a magnetic field range of 0–50 kOe. The superconducting data were obtained from AC susceptibility measurements carried out in the temperature range 2–25 K. The amplitude of applied AC drive signal was 3 Oe and its frequency was 7 Hz. T_c was measured with an accuracy of ±0.1 K. For the T_c and a determination, a powder from the middle layer was taken.

3. Results and discussion

3.1. Combustion velocity

Fig. 2 shows the combustion velocity U as a function of the initial nitrogen pressure $P(N_2)$. It follows that in the investigated pressure range the combustion velocity is slightly varied between 6 and 7.6 mm/s. U seems to attain a maximal value of $U = 7.6 \pm 0.5$ mm/s under $P(N_2) \approx 140$–160 MPa and then to decrease. Such a maximum is quite low expressed however its existence can be expected due to the following consideration. Upon an increase in nitrogen pressure, an increase of nitrogen quantity in the pores of a sample
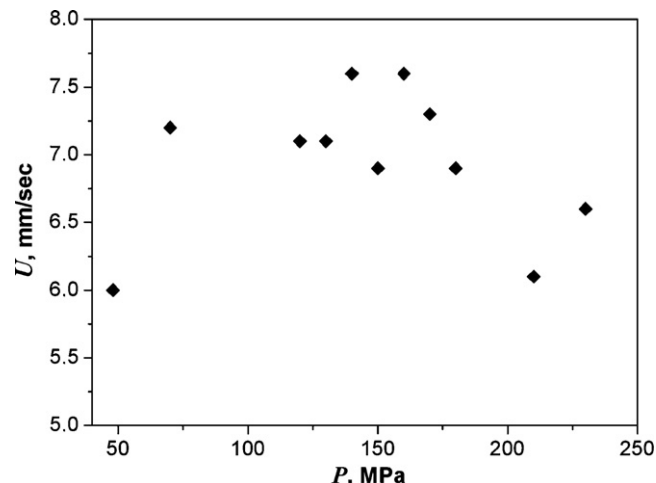

Fig. 1. Schematic of experimental setup: (1) SHS-reactor, (2) tungsten spiral, (3) titanium powder, (4) boron nitride powder, (5) thermocouples and (6) sample.

Fig. 2. Combustion velocity as a function of the initial pressure.
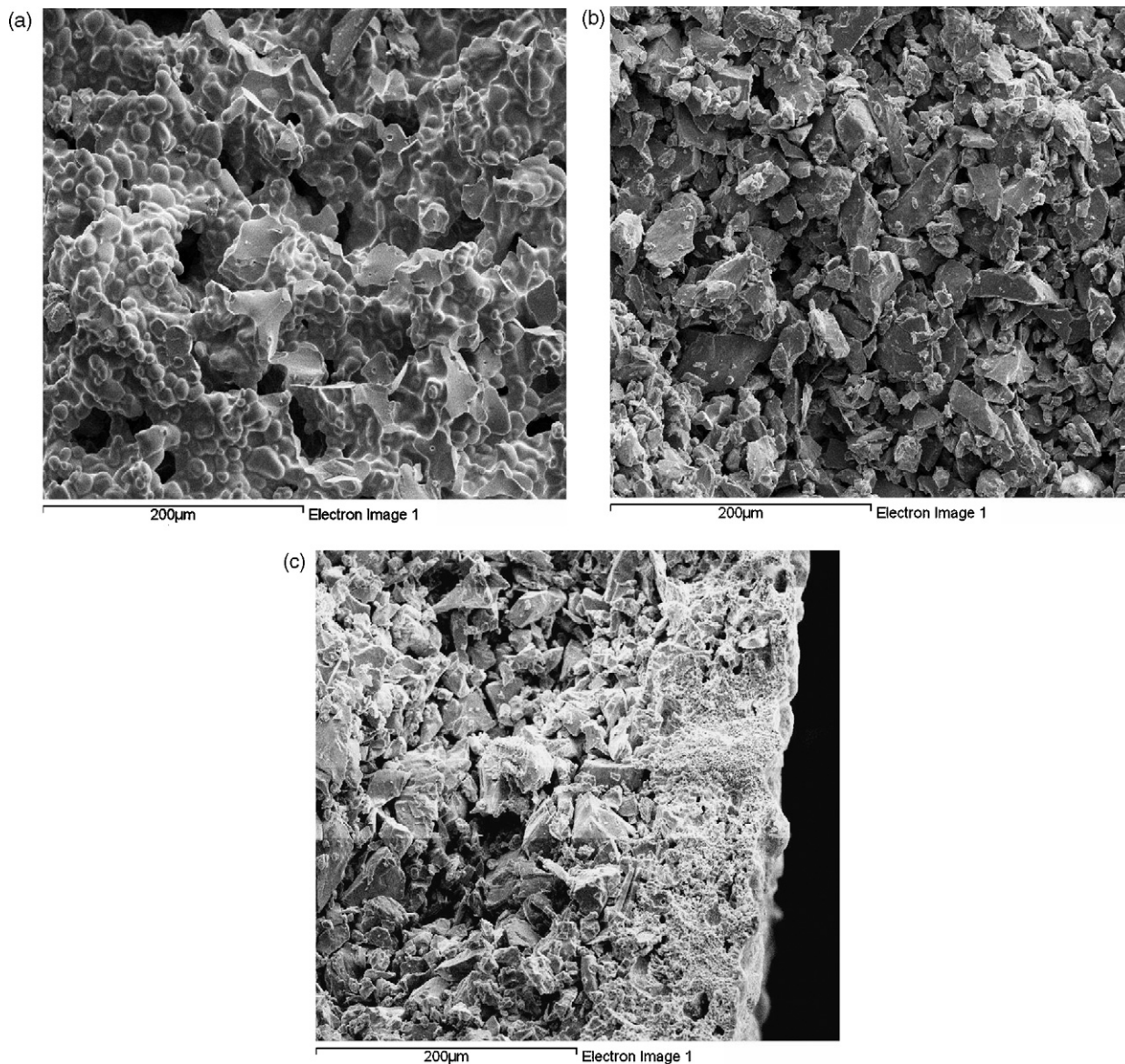
Fig. 3. Microphotograph of the central (a), middle (b) and surface (c) layers of the sample combusted under 230 MPa.

occurs and hence concentration of nitrogen closed to the surface of niobium particles also increases. Due to this, diffusion flux of nitrogen into niobium increases, thus accelerating the nitridation of niobium, which could lead to an increase in the combustion velocity. Decrease in the combustion velocity at pressures higher than 160 MPa is more expressed. The combustion velocity decreases because of an increase of heat loss from the sample into surrounding gas with increasing $P(N_2)$. Such a dependence of U on $P(N_2)$ with a maximum is typical for the Nb–N system and can be more clearly disclosed if being investigated in a pressure range extended to lower pressures (where U intensively increases with pressure increasing). U as a function of $P(N_2)$ with a clear maximum was observed in our previous study [25] where the investigation was made starting from 0.12 MPa.

3.2. Microstructure

Three layers can be visually distinguished in the sample: central (Fig. 3a), intermediate (Fig. 3b) and surface (Fig. 3c). The central layer was 6–8 mm in diameter and consisted of melted product of light yellow color which is typical for cubic niobium nitride.

According to the presented thermogram (Fig. 4), the combustion temperature in the center of a sample (2700–2750 °C) was higher than the melting points of Nb (2469 °C) and of the solid solution of nitrogen in niobium α-Nb ($\sim$2350 °C) [26]. Hence in the micrograph of the central layer of a sample the melted product can be seen. Further towards the surface of a sample, temperature decreases (lower 2350 °C) and the particles preserve the morphology of the starting Nb powder. The surface layer is composed of a thin gray shell 100–150 μm in thickness. The intermediate layer located between the surface and central layers and consisted of not fused light yellow particles of the product.

Melting of the product in the center was observed in the range 70–230 MPa. Under 70 MPa it was less intensive than under higher pressures and the diameter of the central layer was minimal ($\sim$6 mm). Under 48 MPa the sample was not melted and consisted of only two layers: internal and external. The external layer also composed of a thin gray shell (see Fig. 5) and whole the internal layer was similar to the intermediate in Fig. 3b.

According to EDS microanalysis, x in several points of the cross-sections of the central (Fig. 6a) and the intermediate (Fig. 6b) layers achieved 1.12. However the data of such analysis is appreciably
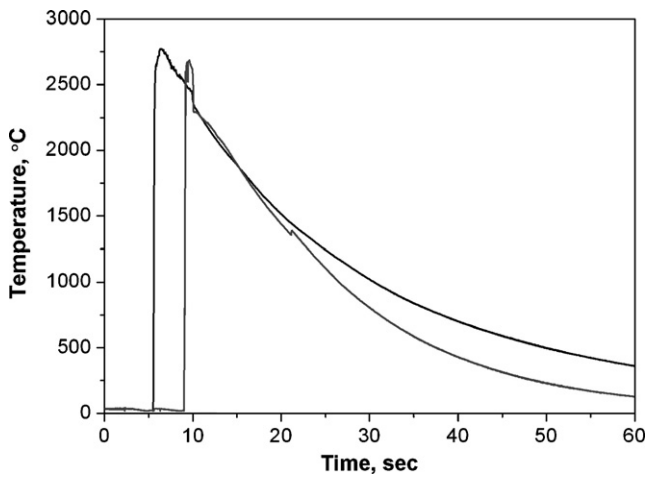
Fig. 4. Thermogram of the sample combusted under 130 MPa.

scattered. In the central layer x is varied in the range 1.03–1.12, while that in the intermediate, in the range 1.015–1.10.

3.3. Nitrogen composition x as a function of P(N₂)

Fig. 7 shows nitrogen composition in the product inferred from weight gain experiments (an increase in weight gain was supposed to occur due to the reaction with nitrogen) as a function of $P(N_2)$. It follows that x initially grows with increasing $P(N_2)$ and attains a maximal value $x = 1.015 \pm 0.01$ under $P(N_2) = 170 \pm 20$ MPa and then decreases with pressure increasing (because of heat loss increasing). Thus according to the weight gain data, a stoichiometric niobium nitride was undoubtedly obtained. However, obtaining of an overly stoichiometric nitride cannot be a priori excluded.

According to chemical analysis, upon variation in a sample radius, nitrogen composition is varied on $\Delta x \approx 0.02$–0.04 on average (see Fig. 8). Meanwhile, x as a function of $P(N_2)$ both in the central (curve 1) and in the intermediate (curve 2) layers reveals a similar dependence to that plotted by the weight gain data. In particular, nitrogen composition in the center is seen also to grow

Fig. 5. Photograph of the sample combusted under 48 MPa.

with increasing $P(N_2)$ and attains a maximal value $x = 1.015 \pm 0.01$ under 170 ± 20 MPa and then decreases with pressure increasing.

The dependence of extent of nitriding on pressure is similar to that of the combustion velocity with the difference that the maximum of $x(P)$ happens under higher pressure $P(N_2) = 170 \pm 20$ MPa than the maximum of $U(P)$ under $P(N_2) = 140$–160 MPa. It can be explained by the fact that the nitridation of Nb occurs not only in the combustion front but also behind it while subsequent cooling of the product (the so-called "afterburning stage").

Almost for all samples nitrogen composition in the center exceeds x in the intermediate layer. It would seem that the melting of a sample has to prevent nitrogen infiltration in the center and thus to result in lower extent of nitriding than in the intermediate layer. However, according to chemical analysis, this does not hap-
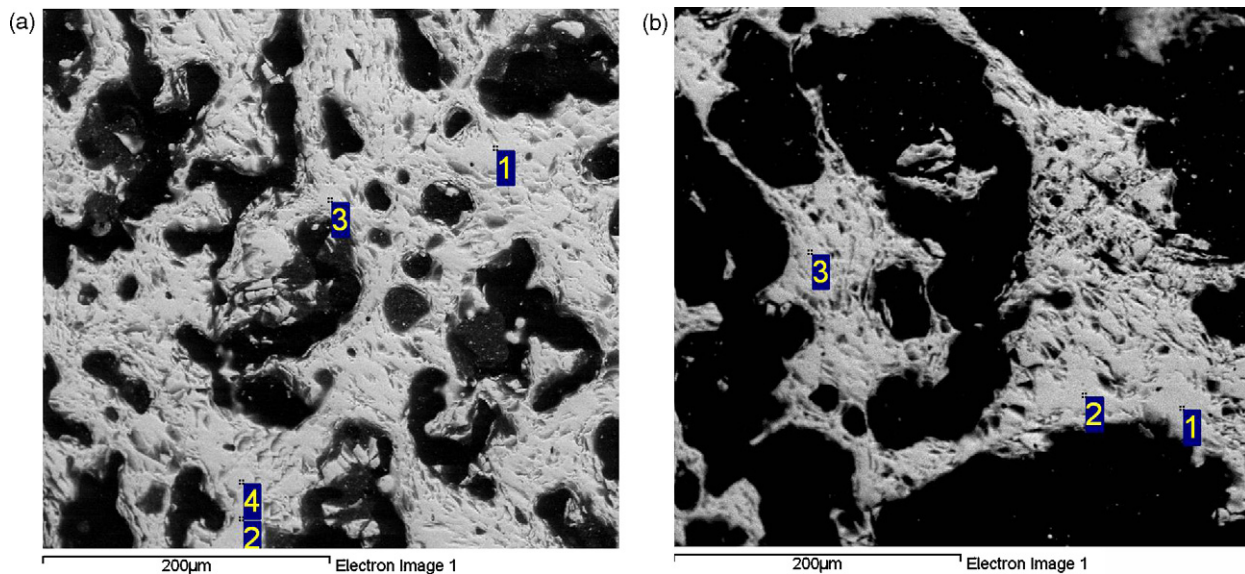

Fig. 6. SEM analysis of the sample combusted under 170 MPa: (a) central layer (point 1: $x = 1.03$; point 2: $x = 1.04$; point 3: $x = 1.09$; point 4: $x = 1.12$) and (b) middle layer (point 1: $x = 1.015$; point 2: $x = 1.03$; point 3: $x = 1.10$).
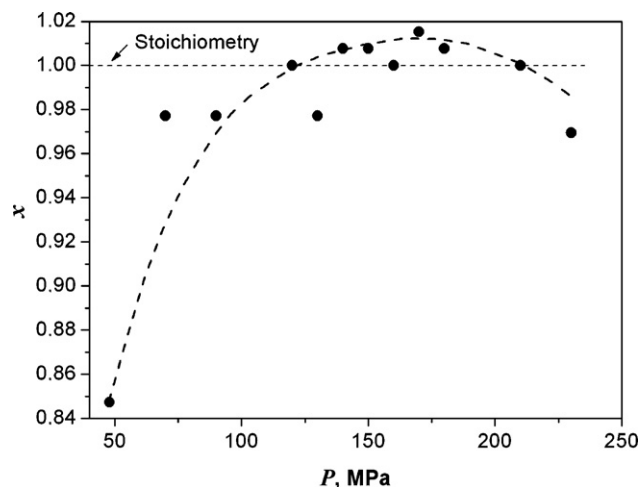
Fig. 7. Stoichiometric coefficient x in NbN$_x$ as a function of $P(N_2)$ inferred from weight gain experiments.

pen that testifies an absence of filtration difficulties or at least their low influence on the final nitrogen distribution in a cross-section of burned sample. On the other hand, before the melting, pores of a sample already contain some quantity of nitrogen which reacts with niobium and thus contributes in the final extent of nitriding. Probably heat loss into surrounding gas is a main factor that effects the final nitrogen distribution in a cross-section of burned sample. In the center heat loss is minimal and due to this the central layer cools down slower than the others. That gives an additional time for the nitridation reaction at high temperature (or for the "after-burning stage") that seems to promote a higher extent of nitriding in the center. Owing to lower heat loss the combustion temperature in the center is higher than in the intermediate and in the surface layers. At higher temperature the diffusion coefficient of nitrogen both into niobium and into its nitrides (such as α-Nb(N), β-Nb$_2$N and δ-NbN) is higher [27,28] that could also promote a higher extent of nitriding of Nb powder in the center.

It should also be noted that in our work [25] on the combustion synthesis of similar Nb samples (15 mm in diameter, 40–50 mm in height and porosity of 51–59%) under $P(N_2) = 0.12–10$ MPa a maximum value $x = 0.94$ was attained (under 8 MPa). Upon deviation from 8 MPa, nitrogen concentration decreased. I.e. neither stoichiometric, no overly stoichiometric niobium nitride was obtained. In [25] the experiments were realized without heat insulation with
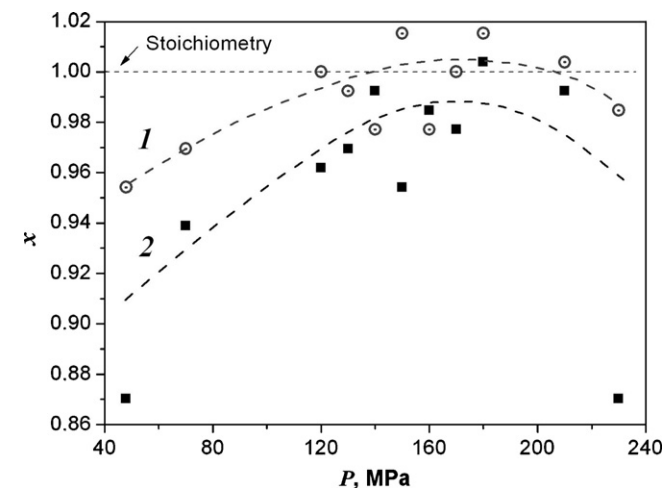

Fig. 8. Stoichiometric coefficient x in NbN$_x$ of the central (curve 1) and the intermediate (curve 2) layers as a function of $P(N_2)$ inferred from chemical analysis.
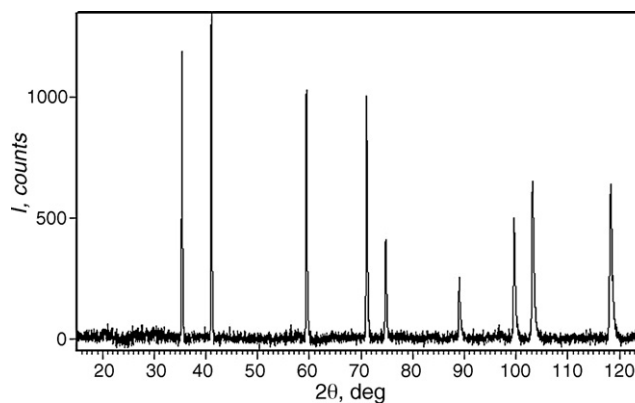

Fig. 9. X-ray diffraction pattern of the product with $x = 0.977$.

BN powder. But in this work, using BN filler both stoichiometry and superstoichiomety was obtained. Thus it can be considered as a good promoter for obtaining higher x.

3.4. XRD analysis

Despite the visual difference between three layers in the sample, both the central and intermediate layers consisted of δ-NbN$_x$. Their diffraction patterns were similar. As an example, Fig. 9 presents the diffraction pattern of the product with $x = 0.977$ (intermediate layer). The surface layer seems to consist of a mixture of δ-NbN$_x$ and niobium carbonitride NbN$_{1-y}$C$_y$ with cubic structure. The peaks of carbonitride in diffraction patterns are similar to those of cubic niobium nitride with the same type of crystal lattice and hence coincide [29]. However, these compounds have different color. That allows us to assume that the surface layer with gray color contains considerable amount of NbN$_{1-y}$C$_y$ in contrast to the internal layers. Carbonitride formation on the surface could be due to the interaction with the pyrolysis products of the filter paper. Meanwhile, the volume fraction of the surface layer composed a minor part of the sample (about 1.3%).

It should also be noted that the phase composition of the surface layer of not melted sample (burned under $P(N_2) = 48$ MPa, see Fig. 5) did not change (as compared with the samples burned under $P(N_2) = 48–230$ MPa) and whole the internal layer consisted of only δ-NbN$_x$.

Meanwhile, the values of lattice parameters of powders from the intermediate layer remain in the range 4.3849–4.3985 Å and some of them exceed that known for δ-NbN$_x$ [5,18,29] ($a_{max} = 4.3934$ Å). Lattice parameter of NbN$_{1-y}$C$_y$ (with any y) is known to have higher value than that of δ-NbN$_x$ [19,29,30]. Thus a minor percentage of carbon in the intermediate layer of some samples seems to exist though. Upon burning, the pyrolysis products of the filter paper evaporated into a gas atmosphere and could be infiltrated with nitrogen to the reaction zone through the pores of the sample.

Fig. 10 shows the $a(x)$ dependence according to the present work (x was determined by chemical analysis, curve 1) and the data of our previous study [18] (curve 2). Our data is in incomplete agreement with that obtained previously since not all the points correspond to δ-NbN$_x$ without impurities. The points with $a > 4.3934$ Å correspond to NbN$_{1-y}$C$_y$ as it was mentioned above.

Oxygen-containing compounds may arise and react with Nb powder in nitrogen atmosphere at high temperatures. The peaks of niobium oxynitride NbN$_{1-z}$O$_z$ with cubic structure also coincide with those of δ-NbN$_x$ and of NbN$_{1-y}$C$_y$ [29]. NbN$_{1-z}$O$_z$ is known to have lower values of lattice parameter ($a_{max} = 4.3896$ Å) than δ-NbN$_x$ and NbN$_{1-y}$C$_y$ [30]. Hence the point with $a = 4.3849$ Å correspond to NbN$_{1-z}$O$_z$ and is in discrepancy with [18]. Taking into
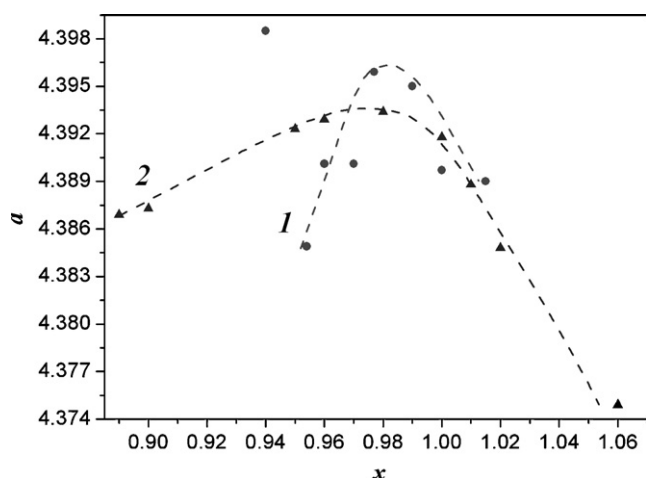
Fig. 10. Lattice parameter a as a function of x: curve (1) present work and curve (2) literature data [18].
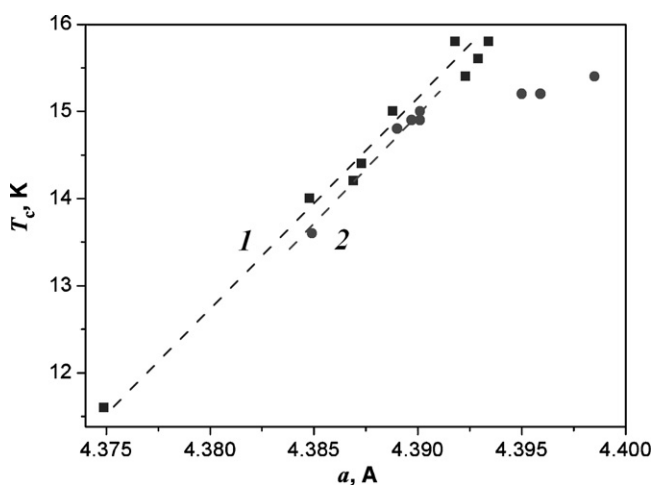

Fig. 11. Critical temperature T_c as a function of a: line (2) present work and line (1) literature data [18].

account the accuracy of determination of x and a in both investigations ($\Delta x = 0.01$, $\Delta a = 0.0005$), the other points can be regarded as agreeing with our previous work [18]. Despite the impurities in the product the data of present investigation is in agreement with [7–9] and also supports the idea that maximal a is exhibited by a slightly off-stoichiometric composition.

3.5. Critical temperature T_c as a function of a

Fig. 11 shows T_c as a function of a: line 1 corresponds to the literature data [18], while line 2, to this work. The behaviour of T_c upon an increase in a in the range of values known for δ-NbN$_x$ ($a_{max} = 4.3934$ Å) is quite similar to the data reported in [18]. However, some points of the present work are in the range $a > 4.3934$ Å and are in discrepancy with [18]. These points seem to correspond not to cubic niobium nitride but to cubic niobium carbonitride. That explains a higher value of a and also a discrepancy with the literature data for δ-NbN$_x$.

Thus for δ-NbN$_x$ a maximal $T_c = 15.0$ K was obtained. This is lower than the T_c values reported in the literature ($T_c = 17.3$ K) [1–3]. In general, a maximum value of $T_c = 15.4$ K was obtained which was found to correspond to the product with maximal lattice parameter $a = 4.3985$ Å.

4. Conclusions

Cubic niobium nitride powders with x both above and below than unity were prepared. A possibility of obtaining of δ-NbN$_x$ with $x \geq 1.00$ via classical SHS without dilution of starting Nb samples with final product was first realized under lower pressures than in [10,11]. It was attained due to applying of special heat conditions. The samples were put into a gas permeable heat insulator of BN powder that gave an additional time for a course of the "after-burning stage" and thus promoted higher extent of nitriding of Nb powder. In order to increase cooling time more, a greater sample size than in [12–17] was used. The combustion product of a greater sample cooled down slower than that of a smaller one.

With increasing a of cubic niobium nitride, T_c linearly grows. This dependence is in a good agreement with the literature data. For δ-NbN$_x$, the maximum value of T_c was found to be 15.0 K.

Acknowledgements

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