Preparation, Composition and Solid State Investigations of TiN, ZrN, NbN and Compounds from the Pseudobinary Systems NbN-NbC, NbN-TiC and NbN-TiN

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Single crystals of the cubic phases TiN, ZrN, δ-NbN and of compounds from the pseudobinary systems NbN-NbC, NbN-TiC, and NbN-TiN were obtained by zone melting, zone annealing and annealing of the metals and metal carbides in nitrogen gas of 2 MPa. Single crystals of the tetragonal phase γ-NbN were obtained in a similar way by annealing of niobium.

The nitrides are non-stoichiometric. TiN was obtained in the composition range $TiN_{0.99}$ to $TiN_{0.50}$, ZrN in the range $ZrN_{1.00}$ to $ZrN_{0.63}$, and the niobium nitrides were obtained in the composition range $NbN_{0.90}$ to $NbN_{0.69}$. The compounds from the pseudobinary systems have up to 35 % vacant sites in the nitrogen-carbon sublattice. TiN and ZrN have only vacant sites in the nitrogen sublattice. A correlation is found between the unit cell parameters for titanium nitride and zirconium nitride and the nitrogen-metal ratios.

The carbides and nitrides of the group IV, V, and VI transition metals have high melting points, and metallic properties such as appreciable thermal and electrical conductivity and metallic lustre. The compounds are hard and brittle. Such properties are not often found in conjunction with appreciable electrical conductivity for refractory materials. Some of the nitrides, all with the sodium chloride structure, are superconductors with moderate to high transition temperatures, the values for T_c are: TiN, 5 K; ZrN, 10K; and δ-NbN, 17.3 K.[1] The generally accepted mechanism for superconductivity is the electron-phonon interaction and it is therefore of great interest to understand the phonon spectra of these compounds.

Inelastic neutron scattering experiments show for some of these transition metal compounds an appreciable difference in the phonon dispersion curves between the compounds that are superconductors and those that are not.[2-5] The anomalies in the phonon dispersion curves are assumed to be due to the strong electron-phonon interactions.

A high temperature crystal growth program was started with the intention to develop reproducible growth methods for the transition metal carbides and nitrides and to make single crystals of these materials available for elastic and inelastic neutron scattering experiments and for other physical investigations. Due to the refractory nature of these compounds, the floating zone crystal growth technique was assumed to be the only method by which large single crystals could be obtained. Growth of transition metal carbides has been reported previously,[6] and large single crystals of titanium carbide have recently been produced using the floating zone technique.[7-9] The preparation of large crystals of the nitrides has not previously been reported in the literature, but has now succeeded during this crystal growth project.[8,9]

The purpose of this paper is to describe the preparation and characterization of crystals of the compounds TiN, ZrN, γ-NbN, δ-NbN, and of compounds from the pseudobinary systems NbN-NbC, NbN-TiC, and NbN-TiN. All these compounds can exist over a rather broad composition range and are normally obtained as non-stoichiometric phases. In the

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following the formulae TiN, ZrN, *etc.* will be used for the non-stoichiometric compounds.

EXPERIMENTAL

Sample preparation and X-ray technique. The crystal growth furnace used was an ADL MP furnace [10] designed to operate at gas pressures up to 2 MPa. The power supply for the furnace was a 30 kW induction generator [11] that operated at 200 kHz. The starting materials were solid rods of the pure metals (Ti and Zr) and powders of the elements and the carbides (Nb, Ti, NbC, TiC). Rods for zone melting experiments were pressed isostatically from powders.[9] The nitrogen used was 99.99 % pure (Dansk Ilt- og Brintfabrik, Copenhagen).

X-Ray diffraction techniques, including Laue back reflection, precession and Guinier powder photography, and optical metallography have been used to characterize the crystals produced. Guinier powder patterns were obtained on all melted and annealed samples using $CuK\alpha_1$ radiation, $\lambda = 1.54051$ Å, or $CoK\alpha_1$ radiation, $\lambda = 1.78892$ Å, with sodium chloride $a_{NaCl} = 5.6389$ Å, or germanium $a_{Ge} = 5.6576$ Å, as internal standards. The specimens were sectioned with a water-cooled diamond cut-off wheel, and the samples were then lapped on a cast iron lap with 400 mesh powder of boron carbide. The lapping was sufficient to make the grain structure of the specimens visible.

TiN. Zone melting of polycrystalline rods of titanium nitride in an ambient nitrogen gas pressure of 2 MPa could not be used in the preparation of single crystals of the compound. The rods expanded and became covered with a porous polycrystalline surface layer and a considerable evaporation started from the heated part of the rod before a molten zone was formed.[9] At temperatures of approximately 3000 K cracks were formed in the surface layer, and through the cracks melted material could be observed. Zone annealing of rods of titanium metal in an ambient nitrogen gas pressure of 2 MPa proved to be a successful method for the preparation of single crystals of titanium nitride. The procedure for a zone annealing is similar to that of a zone melting. A hot zone, and not a molten zone, travels through the specimen at low speed. Large crystal grains are formed during this annealing process. By this method titanium nitride was formed from titanium and nitrogen and the crystals were obtained in one experimental operation. Typical values for the temperature of the heated zone are the range 2000 − 2800 K, and an ambient nitrogen gas pressure of 1 − 2 MPa was normally applied. The crystals had the highest nitrogen content when made at high temperatures and gas pressures. The nitrogen content of the crystals can be raised by annealing of small volumes of single crystals, approximately 0.5 cm³, in ambient nitrogen pressures of 2 MPa and

temperatures in the range 2800 − 2900 K for long periods of time, 65 − 76 h.

ZrN. The main difficulties in the floating zone growth of crystals of ZrN from polycrystalline rods of zirconium nitride were the same as met in the crystal growth of TiN from polycrystalline rods of titanium nitride. A considerable evaporation of ZrN started from the hot, heated part of the specimen before a molten zone was formed, and a porous polycrystalline surface layer of ZrN developed at high temperatures. Through cracks in this surface layer it was possible to observe melted material. − Single crystals of ZrN could be made by zone annealing of zirconium metal in nitrogen gas at 1 − 2 MPa and temperatures in the range 2000 − 2800 K. The crystals had the highest nitrogen content when made at the highest accessible temperatures and gas pressures, and specimens with a composition close to the stoichiometric composition could be made by this method.

NbN. When δ-NbN was zone melted in ambient nitrogen gas pressures of up to 2 MPa specimens were obtained that contained β-Nb₂N and γ-NbN in a lamella structure.[12] In the zone melting nitrogen gas was released from the molten zone. The average composition of a specimen zone melted at an ambient nitrogen gas pressure of 2 MPa was $NbN_{0.69(1)}$ and the feed rod for the zone melting had the composition $NbN_{1.0}$. When a solid bar of niobium metal was annealed in an ambient nitrogen gas pressure of 2 MPa at 2100 K for 110 h a specimen containing twinned crystals of γ-NbN was obtained. The composition of this specimen was $NbN_{0.77(1)}$. Single crystals of δ-NbN were obtained by annealing of small volumes of single crystals of γ-NbN, approximately 0.5 cm³, in ambient nitrogen gas pressures of up to 2 MPa and temperatures in the range 2100 − 2200 K for long periods of time, 90 − 110 h. A single crystal of δ-NbN made by this method had the composition $NbN_{0.90(1)}$.

Compounds from the pseudobinary systems, NbN-NbC, NbN-TiC, and NbN-TiN. Compounds from these pseudobinary systems could be made by zone melting in ambient nitrogen gas pressures of 1 − 2 MPa. In most cases specimens containing cubic single crystals of only one phase were obtained.

Analysis. Determination of the unit cell parameter a showed that the values for a varied within the specimens and also from specimen to specimen in a systematic way, depending upon the experimental conditions used in the crystal growth of the specimens. The variation in a follows the variation in the composition of the metal nitride. The compound TiN_x can exist over a large composition range and an empirical relation between the unit cell parameter a and the ratio N/Ti has been reported.[13] The unit cell parameter is increasing with increasing values of x. As the specimens

showed a systematic variation of a from the surface regions to the centre parts of the specimens, corresponding to a composition gradient, and as nitrogen in TiN cannot be converted quantitatively to NH_3 and determined by this method, it was decided to use the microprobe analysis technique in the determination of the composition and the composition gradients in the specimens of TiN_x. The microprobe analyses were made on a Jeol JXA 50A microprobe operating at an accelerating voltage of 15 kV and a sample current of about 30 nA. Corrections for absorption were made using the procedure of Springer.[14] The titanium contents were determined using 99.99 % Ti and rutile, TiO_2, as standards, and the nitrogen contents were obtained as differences, assuming
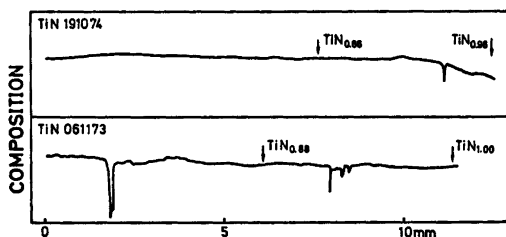

Fig. 1. Composition gradient in two specimens of TiN obtained by scanning along a diameter of a cross sectional slice of the specimens. The composition indicates the metal concentration. The discontinuities in the curves are due to cracks and scratches in the specimens.
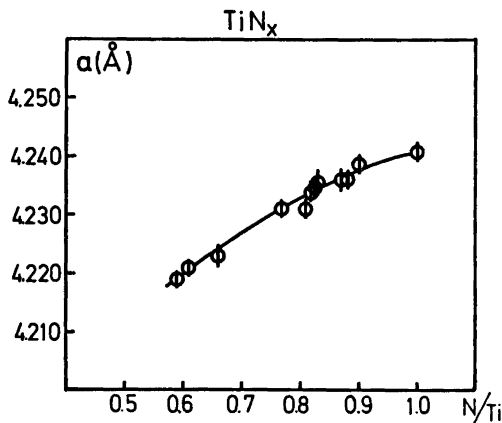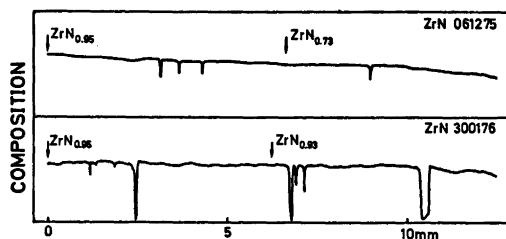

Fig. 3. Composition gradient in two specimens of ZrN obtained by scanning along a diameter of a cross sectional slice of the specimens.

that the specimens contained only the two elements titanium and nitrogen. Fig. 1 illustrates the concentration gradients of two specimens of TiN obtained by scanning along a diameter of a cross sectional slice of the specimens.

The composition of the centre parts of the specimens where the concentration gradients were less pronounced was also determined by gravimetrical analysis. TiN_x was converted quantitatively to TiO_2 by ignition in air at 1000 °C. The samples were placed in Pt-crucibles and kept in an electric furnace for approximately 1 h. Fig. 2 shows the variation in the unit cell parameter a with the composition.

The composition of the specimens of ZrN was also determined by the microprobe analysis technique as described for TiN. In this case 99.99 % Zr was used as a standard. The nature of the concentration gradients for two specimens is shown in Fig. 3. Gravimetrical analysis were made of the centre parts of the
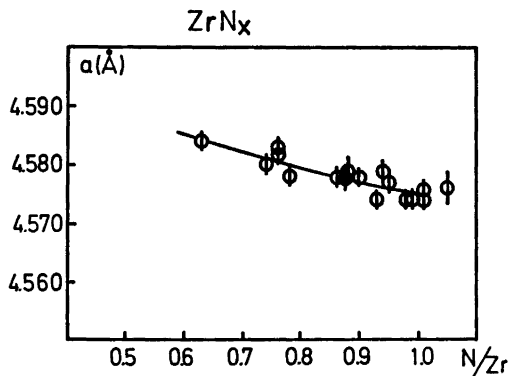

Fig. 2. Correlation between the ratio N/Ti and the unit cell parameter a in TiN_x. The bars indicate the standard deviation on a. Ehrlich[13] has reported the values $a = 4.213$ Å for N/Ti = 0.5 and $a = 4.234$ Å for N/Ti = 1.0. The value for $a = 4.240(1)$ Å at the stoichiometric composition is thus higher than the value published previously.

Fig. 4. Correlation between the ratio N/Zr and the unit cell parameter a in ZrN_x. The bars indicate the standard deviation on a. Rudy and Benesovsky[15] have reported the value $a = 4.577$ Å for N/Zr = 1.0 and $a = 4.584$ Å for N/Zr = 0.5. The values for the unit cell parameter obtained in this investigation are in acceptable agreement with the values reported previously.[15]
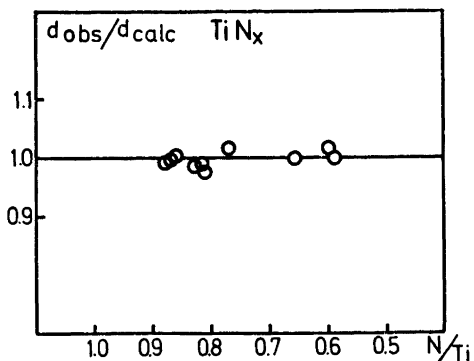
Fig. 5. Display of d_{obs}/d_{calc} vs. x in TiN_x. The standard deviation on d_{obs}/d_{calc} is 0.004. At the stoichiometric composition Ehrlich [13] found 4 % of the lattice sites unoccupied. This is in disagreement with the findings of the present work.
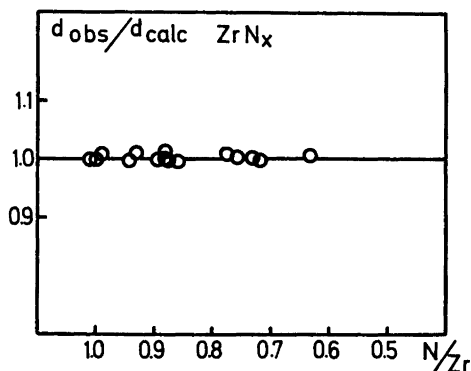

Fig. 6. Display of d_{obs}/d_{calc} vs. x in ZrN_x. Standard deviations on d_{obs}/d_{calc} are 0.003. At approximately $ZrN_{1.0}$ the data of Straumanis, Faunce and James [16] indicate both sublattices contain vacancies. The present work does not support this hypothesis.

specimens. ZrN_x was converted quantitatively to ZrO_2 by ignition in the air at 1180 °C. Fig. 4 shows the variation in the unit cell parameter a with the composition.

The composition of the specimens of niobium nitride was determined gravimetrically by ignition in air at 1000 °C. NbN_x is by this treatment converted quantitatively to Nb_2O_5.

The compounds from the pseudobinary systems NbN-NbC, NbN-TiC, and NbN-TiN were analyzed using the microprobe analysis technique. As standards were used 99.99 % Nb, 99.99 % Ti and TiC and ZrN with known compositions. The specimens were analyzed for Nb, Ti, C, and N. Gravimetrical analyses were also made. (Taking into consideration that the chemical analyses give an average composition of a relatively large volume and the microprobe analyses give compositions of very small volumes of the specimens and often reveal composition fluctuations in the specimens, the two methods of analyses give results in acceptable agreement with each other).

Density determinations. The densities of the

compounds were measured by the method of Archimedes. The densities of the samples of TiN_x and ZrN_x were calculated using values for the composition from the chemical analysis and the unit cell parameter, and assuming that the unit cell contained four formula units of TiN_x or ZrN_x. Figs. 5 and 6 are displays of the ratios between observed and calculated densities vs. the ratios N/Ti and N/Zr, respectively. The densities of the compounds from the pseudobinary systems were calculated in the same way, assuming four formula units in the unit cell.

Magnetic properties. The magnetization of samples of TiN_x and ZrN_x was measured at temperatures from 75 – 300 K using the Faraday method. The samples were placed in a flow cryostat cooled with liquid nitrogen, and the magnetization was recorded with an electrobalance. The magnetic field was calibrated using Mohrs salt, $(NH_4)_2 Fe(SO_4)_2.6H_2O$, $\chi_g = 32.2 \times 10^{-6}$, as a standard. The magnetization varied only 8 % over the temperature range investigated. The magnetic data at 300 K for TiN_x and ZrN_x are listed in Table 1.

Table 1. Magnetic data [a] for TiN_x and ZrN_x.

Compound	χ_{mol}^{-1}	Compound	χ_{mol}^{-1}	Compound	χ_{mol}^{-1}
$TiN_{0.99}$	142.8	$TiN_{0.82}$	19.3	$TiN_{0.59}$	24.8
$TiN_{0.90}$	37.9	$TiN_{0.77}$	32.6	$ZrN_{0.88}$	50.0
$TiN_{0.87}$	43.2	$TiN_{0.66}$	18.0	$ZrN_{0.88}$	38.4
$TiN_{0.83}$	32.7	$TiN_{0.61}$	33.5	$ZrN_{0.72}$	18.3

[a] χ_{mol}^{-1} determined for magnetic field 3000 Gauss.

RESULTS AND DISCUSSION

The investigation shows that large single crystals can be made of TiN, ZrN, of the niobium nitrides γ-NbN and δ-NbN, and of compounds from the pseudobinary systems NbN-TiC, NbN-TiN, and NbN-NbC. These compounds from the pseudobinary systems can be obtained by the floating zone crystal growth technique. Large single crystals of vanadium nitride, VN, can also be made by this growth method.[17] Single crystals of TiN and ZrN are made by the zone annealing technique. The annealing technique was applied in the preparation of crystals of γ-NbN and δ-NbN. This method was also used to increase the nitrogen content in specimens of TiN and ZrN made by the zone annealing technique.

Specimens of TiN and ZrN prepared by the zone annealing method show a composition gradient from the surface to the centre of the rods. This composition gradient can be determined by the microprobe analysis method and by chemical analysis. The surface layers have higher nitrogen contents than the centre regions. The nitrides are formed in the solid state and the formation is governed by diffusion of nitrogen from the surface layers to the centre regions of the rods. Many specimens had a yellow colour of the surface layers and a metallic white colour of the centre regions corresponding to compositions close to the stoichiometric compositions of the surface layers and composition far from stoichiometry of the centre regions.

The composition of the specimens of TiN and ZrN is dependent upon the preparative parameters temperature, time and nitrogen gas pressure. Specimens kept at the highest temperatures and gas pressures for the longest periods of time had the highest nitrogen contents. TiN was obtained as single crystals within the composition range $TiN_{0.99}$ to $TiN_{0.50}$, and ZrN was obtained as single crystals within the composition range $ZrN_{1.00}$ to $ZrN_{0.63}$.

Empirical relations have been found between the unit cell parameter a and the composition for TiN_x and ZrN_x (see Figs. 2 and 4). The parameter a for TiN_x is increasing with increasing values for x. From the crystal structure of ε-TaN [18] the radius for N of 0.708(3) Å in a metal nitride is obtained. This is in good

agreement with previously reported values of 0.71 Å.[19] For a metal nitride with the NaCl structure the densest packing is obtained when $r_N/r_M = 0.4142$, or when $r_M = 1.71$ Å. With increasing values of x the unit cell parameter a should increase when $r_M < 1.71$ Å, in that case the volume of a vacant site would be smaller than that of a nitrogen atom. This is the case for Ti, $r = 1.467$ Å, as well as for Zr, $r = 1.597$ Å (values listed for coordination number 12 in Ref. 1). The effect is observed for TiN_x but not for ZrN_x. It is assumed that the metal nitride has an appreciable metal-nitrogen bonding contribution to the chemical bonds of the compounds. When the nitrogen content is increased in ZrN_x the number of $Zr-N$ bonds is increased and if this type of interaction is comparable with or even stronger than the $Zr-Zr$ and the $N-N$ interactions, the lattice will contract. This effect is apparently dominating over the vacancy filling effect of the nitrogen sublattice in ZrN_x. The heat of formation of ZrN is numerically larger than that of TiN.[1] It is thus tempting to assume that ZrN has stronger bonds than TiN.

For compounds showing superconductivity at low temperatures, it is normally found that the transition temperature T_c has its highest value for specimens with a stoichiometric composition, and the values of T_c fall with an increasing deviation from the stoichiometric composition. For the compounds TiN_x and ZrN_x with the sodium chloride structure it is evident that non-stoichiometric TiN_x and ZrN_x with $x < 1.0$ will have vacant lattice points on the nitrogen sublattice. The metal sublattice may be filled, or may have vacant lattice positions as well. In the compound TiO it is found that each of the two sublattices have 15.5 % vacant lattice sites for the stoichiometric composition $Ti_{1.0}O_{1.0}$.[20] This is due to an ordering of the vacant sites in the two sublattices so the symmetry of the crystal is changed from cubic to monoclinic. TiO shows no superconductivity at low temperatures. For TiN it is likely that the two sublattices are filled when the compound has the stoichiometric composition. This can be made probable by making a comparison of observed and calculated densities. The densities for the samples of TiN_x were calculated using the values for the composition and the unit cell

parameter, and assuming that the unit cell contained four formula units of TiN_x. This corresponds to a filled titanium sublattice and a nitrogen sublattice with vacant sites. Fig. 5 is a display of the ratios between observed and calculated densities vs. the ratios N/Ti. This shows that the values for d_{obs}/d_{calc} cluster round the value 1.0 in the composition range investigated. It is thus most likely that the two sublattices in TiN are filled at the stoichiometric composition $Ti_{1.0}N_{1.0}$.

The densities for the specimens of ZrN_x were also calculated using the values for the composition obtained from the chemical analysis and the unit cell parameter, and assuming that the unit cell contained four formula units of ZrN_x. This corresponds to a filled zirconium sublattice and a nitrogen sublattice with vacant sites. Fig. 6 is a display of the ratios between observed and calculated densities vs. the ratio N/Zr. This shows that the values for d_{obs}/d_{calc} cluster around the value 1.0 in the composition range investigated. It is thus most likely that the two sublattices in ZrN are filled at the stoichiometric composition $Zr_{1.0}N_{1.0}$. The superconductivity of the two stoichiometric nitrides TiN and ZrN also supports the assumption that the metal sublattices are filled at the stoichiometric compositions.

The investigation of the magnetic properties of TiN and ZrN shows that the compounds have field dependent values for X_{mol}^{-1}. A tendency is observed for increasing values of X_{mol}^{-1} with increasing values of the ratio N/M, but the data does not give a clear picture of this relation between X_{mol}^{-1} and N/M. The large scatter in the data may be due to different contents of paramagnetic impurities in the specimens. (The nitrides were prepared from metals obtained from different suppliers).

The zone melting experiments on δ-NbN with an almost stoichiometric composition all resulted in specimens containing γ-NbN and β-Nb$_2$N. By increasing the ambient nitrogen gas pressure to 2 MPa it was possible to reduce the quantity of β-Nb$_2$N in the specimens considerably compared with the content of β-Nb$_2$N in specimens made by zone melting with nitrogen gas pressures less than 0.5 MPa. However, by increasing the nitrogen gas pressure to 2 MPa it was not possible to obtain specimens of pure γ-NbN, as these specimens

always contained a minor quantity of β-Nb$_2$N. The zone melting growth technique was thus not adequate for the preparation of the pure phases δ-NbN, γ-NbN, and β-Nb$_2$N. This is in contrast to the zone melting of sintered rods of δ-VN in an ambient gas pressure of 2 MPa, that gave single crystals of δ-VN with compositions in the range $VN_{0.74}$ to $VN_{0.86}$.[17] Zone melting of sintered rods of δ-VN in an ambient nitrogen gas pressure of 1 MPa yielded specimens containing β-V$_2$N and δ-VN in a lamella structure.[21] An ambient nitrogen gas pressure of 2 MPa is thus sufficient to keep the composition of a melt of vanadium nitride within a composition range where δ-VN is the stable solid phase but is insufficient to keep the composition of a melt of niobium nitride within a composition range where δ-NbN is the stable solid phase.

Annealing of niobium or niobium nitride in pure nitrogen at temperatures over 2000 °C resulted in the formation of the pure phase γ-NbN. However, the crystals of γ-NbN in the specimens were twinned. Annealing of small samples of γ-NbN (volumes approximately 0.5 cm^3) at 2100 − 2200 °C and ambient nitrogen gas pressures of up to 2 MPa for long periods of time, approximately 100 h, resulted in an increase of the nitrogen content of the specimens. Cubic single crystals of δ-NbN formed in this annealing growth process could be cooled to room temperature without undergoing the phase transition[12] to γ-NbN. The fast cooling from temperatures above 1800 °C that was used in the formation of polycrystalline rods of δ-NbN[22] could thus also be used in the formation of single crystals of δ-NbN. In one annealing experiment where the specimen had a volume of approximately 1 cm^3 a single crystal of γ-NbN was obtained. The annealing time used for this experiment has possibly been too short to insure a sufficiently high nitrogen content in the specimen to avoid the phase transition from δ-NbN to γ-NbN during the cooling process.

Typical values for the composition of niobium nitrides obtained by the different preparative methods are listed in Table 2.

Single crystals of compounds belonging to the pseudobinary systems NbN-TiC, NbN-TiN, and NbN-NbC have been made using the floating zone crystal growth technique. Results

Table 2. Composition and unit cell parameters of niobium nitrides. (Standard deviations in parentheses).

Method of preparation	N_2 gas pressure in MPa	Temp. in °C	Time h	Composition from chemical analysis	Product	Unit cell parameter in Å
Zone melting of δ-NbN	1.95	>2100	13	$NbN_{0.69(1)}$	γ-NbN	$a=4.380(1)$ [a] $c=4.303(1)$
					β-Nb$_2$N	$a=5.279(2)$ $c=4.990(2)$
Annealing of Nb in N_2	2.00	2100	112	$NbN_{0.77(1)}$	γ-NbN	$a=4.392(2)$ [a] $c=4.317(3)$
Annealing of γ-NbN in N_2	2.00	2100	96	$NbN_{0.90(1)}$	δ-NbN	$a=4.377(1)$
Fast reaction between Nb and N_2 (Ref. 18)	2.00	>1800	20 20 s	$NbN_{0.98(2)}$ [b]	δ-NbN	$a=4.394(3)$

[a] Small unit cell used. [b] From neutron diffraction.

Table 3. Composition, unit cell parameters and densities of single crystals from NbN-MeX systems. [c]

Exp. No.	Composition from analysis	Unit cell parameter in Å	d_{obs} g cm^{-3}	d_{calc} [b] g cm^{-3}	d_{obs}/d_{calc}
1.	$Nb_{0.84}Ti_{0.16}N_{0.67}C_{0.10}\square_{0.23}$	4.360(2)	7.566	7.716	0.981
2.	$Nb_{0.83}Ti_{0.17}N_{0.61}C_{0.10}\square_{0.29}$	4.362(2)	7.612	7.602	1.001
3.	$Nb_{0.83}Ti_{0.17}N_{0.70}\square_{0.30}$	4.361(2)	7.751	7.612	1.018
4.	$Nb_{0.91}Ti_{0.09}N_{0.57}C_{0.11}\square_{0.32}$	4.380(2)	7.826	7.759	1.009
5.	$Nb_{0.83}Ti_{0.17}N_{0.65}C_{0.05}\square_{0.30}$	4.336(3)	7.637	7.737	0.987
6.	$Nb_{0.85}Ti_{0.15}N_{0.63}C_{0.10}\square_{0.27}$	4.358(2)	7.523	7.718	0.975
7.	$Nb_{0.83}Ti_{0.17}N_{0.78}\square_{0.22}$	4.343(2)	7.809	7.731	1.010
8.	$Nb_{0.83}Ti_{0.17}N_{0.77}C_{0.05}\square_{0.18}$	4.346(1)	7.857	7.819	1.005
9.	$Nb_{1.00}N_{0.56}C_{0.14}\square_{0.30}$	4.397(2)	8.011	8.003	1.001
10.	$Nb_{1.00}N_{0.55}C_{0.13}\square_{0.32}$	4.388(3)	8.034	8.032	1.000
		$a=4.390(1)$ [a]			
11.	$Nb_{1.00}N_{0.72}C_{0.03}\square_{0.25}$	$c=4.331(1)$	8.155	8.224	0.992
12.	$Nb_{1.00}N_{0.58}C_{0.07}\square_{0.35}$	4.380(1)	8.135	8.052	1.010
13.	$Nb_{1.00}N_{0.58}C_{0.10}\square_{0.32}$	4.393(2)	8.053	8.009	1.006
14.	$Nb_{1.00}N_{0.52}C_{0.16}\square_{0.32}$	4.403(1)	7.971	7.945	1.003
15.	$Nb_{1.00}N_{0.51}C_{0.17}\square_{0.32}$	4.406(2)	7.909	7.927	0.998
16.	$Nb_{1.00}N_{0.51}C_{0.19}\square_{0.30}$	4.420(2)	7.885	7.871	1.002

[a] Tetragonal. [b] Calculated from chemical and microprobe analysis. [c] Standard deviations of a in parentheses. Typical values of standard deviations for d_{obs}, d_{calc}, and d_{obs}/d_{calc} are 0.015, 0.015, and 0.003, respectively.

of these growth experiments are listed in Table 3. Growth experiments resulted in samples containing single crystals. Systems containing niobium nitride and niobium carbide or other transition metal carbides and nitrides have been reported to have compounds with moderate to high transition temperatures for super-

conductivity. For compounds from the systems NbN-TiC and NbN-NbC reported values are: $(NbN)_{0.8}$ $(TiC)_{0.2}$, 18.0 K; and $(NbN)_{0.7}$ $(NbC)_{0.3}$, 17.8 K.[1]

By addition of transition metal carbides and nitrides to NbN it has thus been possible to obtain cubic phases, and the phase transition

observed for pure niobium nitride from δ-NbN to γ-NbN on cooling is thus suppressed. For the pseudobinary system NbN-NbC it was found that zone melting of a specimen with the nominal composition $Nb_{1.0}N_{0.9}C_{0.1}$ resulted in a sample of a tetragonal phase with unit cell parameters similar to the unit cell parameters of γ-NbN. For the systems addition of NbC, TiC, and TiN in a quantity corresponding to a mol fraction of 0.2 was sufficient to insure the formation of cubic crystals. It is assumed that the high values for T_c are connected with the cubic structure of these materials and increasing values of T_c should be expected for specimens with compositions approaching the stoichiometric composition. The results of chemical analysis, microprobe analysis and density determinations listed in Table 3 indicate that the crystals of these compounds are non-stoichiometric, and it is most likely that the nitrogen-carbon sublattice has up to 35 % vacant sites, with the metal sublattice being filled.

Investigations of the superconducting properties of single crystals obtained in this crystal growth project are planned, and the results will be published elsewhere. Measurements of the phonon dispersion curves for TiN,[23] ZrN,[24] VN, and δ-NbN are in progress.

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