Some Features of the Nb-N and Nb-N-O Systems

NILS SCHÖNBERG

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

I. THE Nb-N SYSTEM

In 1952 Brauer and Jander [1] published a paper on the phases in the niobium - nitrogen system. In order to facilitate comparison of their results and those attained in the present investigation, the following data are recorded from their paper:

Nb dissolves up to about 2 at.-% of N, the lattice constant increasing from $a = 3.301$ Å to $a = 3.303$ Å.

The $NbN_{0.40-0.50}$ phase is of the common "interstitial" structure type with the metal atoms hexagonally close-packed. The unit cell dimensions vary from $a = 3.056$ Å, $c = 4.956$ Å, $c/a = 1.622$ ($NbN_{0.40}$) to $a = 3.048$ Å, $c = 4.995$ Å, $c/a = 1.639$ ($NbN_{0.50}$).

The $NbN_{0.75-0.79}$ phase has a tetragonally deformed NaCl structure. The a-axis increases from 4.385 Å to 4.387 Å, and the c-axis from 4.312 Å to 4.330 Å ($c/a = 0.983$—0.987).

The $NbN_{\sim 0.87 - \sim 0.94}$ phase — NbN III — is of the NaCl type with the cubic axial length $a = 4.39$ Å.

The metal atoms in the $NbN_{\sim 0.95}$ phase — NbN II — form a hexagonal close-packed unit cell with the dimensions $a = 2.94$ Å, $c = 5.46$ Å, $c/a = 1.87$.

The phase most rich in nitrogen has the composition NbN — NbN I — and contains four formula units NbN. The lattice constant of the hexagonal unit cell are: $a = 2.956$ Å, $c = 11.275$ Å, $c/a = 3.815$. The metal positions are given as: 0, 0, 0; 0, 0, $\frac{1}{4}$; 2/3, 1/3, 1/2; 2/3, 1/3, 3/4.

Brauer and Jander point out that the phases mentioned above are pure nitrides but report many specimens containing a small amount of oxygen. For instance, two samples with the composition $NbN_{0.76}O_{0.09}$ and $NbN_{0.88}O_{0.10}$ have the NaCl structure, and a sample with the composition $NbN_{0.75}O_{0.03}$ has the tetragonally deformed version of this structure.

Experimental

The nitrides were prepared by nitriding niobium metal powder (Fansteel) or niobium hydride (Metal Hydrides Inc.) with dry oxygen-free ammonia at various temperatures between 700° C and 1 100° C and for periods varying between one hour and two weeks.

The phase analysis and structure determinations were made from powder photographs taken with Cu$K\alpha$ radiation in cameras of Guinier type using bent quartz and aluminium monochromators. For measurements of the high-angle reflections additional photographs were taken with focusing cameras of Hägg-Phragmén type.

The nitrogen content of the samples was determined by means of the Kjeldahl method.

α phase: Nb(N)

The solubility of nitrogen in the niobium lattice is very small, and could not be determined with any accuracy. The increase in the lattice constant agrees with the results given by Brauer and Jander.

β phase: $NbN_{0.40-0.50}(Nb_2N)$

The results obtained in the present investigation confirm the data given by Brauer and Jander.

γ phase: $NbN_{\sim 0.80 - \sim 0.90}$

Powder photographs of nitrides with the composition varying between $NbN_{0.50}$ and $NbN_{0.80}$ showed besides the pattern of the β phase, diffraction lines of a new phase (γ). A sample with the composition $NbN_{0.86}$ contained this phase in a pure state. The γ phase was found to be isomorphous with the δ phase in the Ta-N system [2], *i.e.* of the WC type [3]. The unit cell dimensions vary between $a = 2.950$ Å, $c = 2.772$ Å, $c/a = 0.940$ ($V = 20.89$ Å^3) and $a = 2.958$ Å, $c = 2.779$ Å, $c/a = 0.939$ ($V = 21.06$ Å^3). The approximate phase limits were found to be $NbN_{0.80}$ and $NbN_{0.90}$. From space considerations the most likely position of the nitrogen atom must be at one of the centres of the two trigonal metal atom prisms in the unit cell. The space-group is D_{3h}^1—$P\bar{6}m2$ with 1 Nb in 1(a) 0, 0, 0 and 1 N in 1(d) 1/3, 2/3, 1/2 or 1(f) 2/3, 1/3, 1/2.

In the region $NbN_{0.75-0.94}$ Brauer and Jander report the existence of two phases, *viz.* $NbN_{0.75-0.79}$ with a tetragonally deformed NaCl structure and $NbN_{\sim 0.87 - \sim 0.94}$ with NaCl structure. No traces of these phases were visible in the photographs. Oxidation of nitrides, however, caused the formation of these compounds, so in all probability they belong to the ternary Nb—N—O system (see below).

δ phase: $NbN_{\sim 0.95}$

This phase is identical with the compound NbN II reported by Brauer and Jander.

The unit cell dimensions were found to be: $a = 2.968$ Å, $c = 5.535$ Å, $c/a = 1.865$ ($V = 42.22$ Å^3). The nitrogen atoms are probably located at the centres of metal atom octahedra. The space-group is thus D_{6h}^4—$P6_3/mmc$, with the atoms in the positions: 2 Nb in 2(c) 1/3, 2/3, 1/4; 2/3, 1/3, 3/4 and 2 N in 2(a) 0, 0, 0; 0, 0, 1/2, *i.e.* the "anti-NiAs" configuration.

ε phase: $NbN_{1.00}$

The present investigation confirmed the metal atom positions reported by Brauer and Jander.

The hexagonal lattice constants were invariably found to be $a = 2.952$ Å, $c = 11.25$ Å, $c/a = 3.811$ ($V = 85.09$ Å^3). If the nitrogen atoms are assumed

to be located at the centres of metal atom octahedra giving the largest N-N distances, the space-group is D_{6h}^4—$P6_3/mmc$, with the atomic grouping: 4 Nb in 4(f) 1/3, 2/3, z; 2/3, 1/3, $\bar{z}$; 2/3, 1/3, $\frac{1}{2} + z$; 1/3, 2/3, $\frac{1}{2}$—z with z = 1/8, 2 N in 2(a) 0, 0, 0; 0, 0, 1/2, and 2 N in 2(d) 1/3, 2/3, 3/4; 2/3, 1/3, 1/4. Three analogous compounds have been prepared earlier, viz. MoC(γ') [4], TiP [2], and β-ZrP [2]. It should be particularly noted that the present author was able to determine the above positions for the nonmetal atoms in the two phosphide phases.

  If the projections of the positions of the atoms on the basal planes of the trigonal or hexagonal γ, δ, and ε phases are designated by A, B, and C, the niobium lattice in the three compounds can be symbolized by the sequences AA . . ., ABAB . . ., and AABBAABB . . . respectively. If the nitrogen atoms also are taken into consideration the resulting stacking sequences are $A_{Nb}B_N$. . ., $A_{Nb}C_NB_{Nb}C_N$ . . ., and $A_{Nb}B_NA_{Nb}C_NB_{Nb}A_NB_{Nb}C_N$ . . . It is remarkable that no contraction takes place along the c-axis when the contact AA in the γ-phase changes to the contact AB in the δ and ε phases ($c_\gamma \sim c_\delta/2 \sim c_\varepsilon/4$). The length of the a-axis also varies little for the three nitrides — between 2.950 Å and 2.968 Å. The value of the axial ratio for the δ phase is c/a = 1.87, while the corresponding value for the β phase is c/a = 1.63 (= $\sqrt{8/3}$). The last value is characteristic for a hexagonal close-packed arrangement of metal atoms. The large deviation must be due to the presence of approximately two nitrogen atoms in the unit cell of the δ phase instead of one in the β phase. The N-N distances always exceed a value of 2.6 Å in metallic nitrides, which can be explained by a displacement of electrons from the transition metal to the nonmetal atom, so that the metal-nitrogen bonds have a partial ionic character.

The mean interatomic distances are listed in Table 1.

Table 1. Mean interatomic distances in niobium nitrides.

Phase	Atom	Surrounding atoms	Interatomic distance, Å
β	Nb	12 Nb 3 N	3.05 2.16
	N	6 Nb	2.16
γ	Nb	2 Nb 6 Nb 6 N	2.78 2.95 } 2.87 2.20
	N	6 Nb	2.20
δ	Nb	6 Nb 6 Nb 6 N	2.97 3.26 } 3.11 2.20
	N	6 Nb	2.20
ε	Nb	1 Nb 6 Nb 3 Nb 6 N	2.81 2.95 } 3.04 3.29 2.21
	N	6 Nb	2.21

The nitrides of the group Va metals

The Me-N systems with Me = a transition element in group Va (V, Nb, Ta) exhibit great similarities for a low nitrogen content, but discrepancies for a high one. The solubility of nitrogen in the metal lattices is of the order 2 at.-% The "interstitial" structure type Me_2N with the metal atoms hexagonally close-packed and the nitrogen atom in one of the two metal atom octahedra of the unit cell (L'3 type) is common for the three Me-N systems *. This phase has a comparatively broad homogeneity range, with the upper phase limit closely corresponding to the composition Me_2N. There exist with the greatest probability a continuous solid solution series V_2N—Nb_2N—Ta_2N. — The $NbN_{0.8-0.9}$ and $TaN_{0.8-0.9}$ phases are isomorphous, while no analogous V-N phase exists. — The atomic grouping for the ε phase in the NbN system can be regarded as a transitionary state between the arrangement of atoms in the γ and δ phases. — VN and NbN are of the NaCl and γ'-MoC [4] types respectively. The structure of TaN [2] is of the B 35-type. The hexagonal unit cell contains three formula units TaN in the space-group D^1_h—$P6/mmm$ with 1 Ta in 1(a) 0, 0, 0, 2 Ta in 2(d) 1/3, 2/3, 1/2; 2/3, 1/3, 1/2 and 3 N in 3(f) 1/2, 0, 0; 0,1/2, 0; 1/2, 1/2, 0.

II. THE Nb—N—O SYSTEM

Ammonia nitriding of niobium oxides or ammonium niobate lead to the formation of a phase of NaCl type. The nitrogen content was determined by the Kjeldahl method, the niobium content by weighing the Nb_2O_5 formed after oxidation by oxygen, and the oxygen content as the weight remainder. The composition of this phase was found to vary slightly about the approximate composition $NbN_{0.9}O_{0.1}$. The length of the cube edge varies between $a = 4.373$ Å ($V = 83.62$ Å³) and $a = 4.390$ Å ($V = 84.60$ Å³). The same compound was

Table 2. Mean interatomic distances in metallic niobium oxide-nitrides.

Phase	Atom	Surrounding atoms	Interatomic distance, Å
$NbN_{\sim0.9}O_{\sim0.1}$	Nb	12 Nb 6 (N, O)	3.10 2.19
	(N, O)	6 Nb	2.19
$NbN_{\sim0.6}O_{\sim0.3}$	Nb	6 Nb 6 Nb 3 (N, O) 3 (N, O)	3.08 } 3.09 3.10 2.16 } 2.17 2.19
	(N, O)	3 Nb 3 Nb	2.16 } 2.17 2.19

* A report on the V—N system was published by Hahn [5] in 1949. An X-ray investigation of the same system carried out by the present author confirmed in all respects the data given by Hahn. Recently, Rostoker and Yamamoto [6] reported the existence of a nitride isomorphous with the tetragonal $VO_{\sim0.15-\sim0.25}$ phase [7]. The preparation methods used by these authors indicate that they obtained oxides instead of nitrides, however.

also obtained from the oxidation of NbN (δ or ε) with steam in the presence of hydrogen in great excess at a temperature of about 700° C. This oxidation process also gave rise to a phase with a tetragonally deformed NaCl structure. The same compound was obtained if $Nb_{0.8-0.9}$ (γ) was used as starting material. The composition of this oxide-nitride was found to vary between the approximate limits $NbN_{0.6}O_{0.2}$ and $NbN_{0.6}O_{0.3}$, with the unit cell dimensions $a = 4.370$ Å, $c = 4.295$ Å, $c/a = 0.983$ ($V = 82.03$ Å³) and $a = 4.386$ Å, $c = 4.325$ Å, $c/a = 0.986$ ($V = 83.21$ Å³) respectively.

No other ternary metallic phases seem to exist in the Nb-N-O system, as oxidation of nitrides with steam for prolonged periods only lead to the formation of already known niobium oxides [8].

Interatomic distances are listed in Table 2.

As was mentioned earlier, it was not possible to prepare the two phases with NaCl and tetragonally deformed NaCl structure in an oxygen-free state.

SUMMARY

The Nb-N system and the part of the Nb-N-O system with the (N,O)/Nb ratio ≤ 1 have been examined by X-ray methods. The following phases have been found to exist:

I. *The Nb-N system*
α phase. The solubility of nitrogen in the niobium metal lattice is probably of the order 2 at.-%.
β phase. Homogeneity range $NbN_{0.40-0.50}$. Metal atoms hexagonally close-packed.
γ phase. Homogeneity range $NbN_{0.80-0.90}$. WC type.
δ phase. $NbN_{\sim 0.95}$. Metal atoms hexagonally closepacked but with $c/a = 1.87$.
ε phase. NbN of γ'-MoC type.
II. *The Nb-N-O system*

Two metallic ternary phases have been observed: $NbN_{\sim 0.9}O_{\sim 0.1}$ with NaCl structure and $NbN_{\sim 0.6}O_{\sim 0.3}$ with a tetragonally deformed NaCl structure.

The Me-N systems with Me = a group Va metal have been compared.

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