The Crystal Structure of ScNbN$_{1-x}$ and Comparisons with Related Nitride and Carbide Structures

WALTER LENGAUER

Institute for Chemical Technology of Inorganic Materials, Technical University of Vienna, Getreidemarkt 9, A-1060 Vienna, Austria

A ternary nitride phase, ScNbN$_{1-x}$, was prepared by nitridation of Sc–Nb alloys. X-ray powder diffraction analysis yielded the following structure model: space group $P6_3/mmc$ (No. 194) with the lattice parameters $a = 0.30633(6)$ and $c = 1.05702(35)$ nm; 2 Sc atoms in 2(a), 2 Nb atoms in 2(d), and 4 N atoms in 4(f) with $z \approx \frac{1}{8}$ and a random occupancy of 50%. The stacking sequence of the metal atoms can be described by ABAC, ABAC, ... The structure can be described as an anti-TiAs-type structure. Several similarities between the ScNbN structure and those of binary and ternary nitride and carbide phases are discussed. © 1989 Academic Press, Inc.

1. Introduction

A ternary phase ScTaN$_{1-x}$ was observed recently (*1*). From a structural viewpoint, this phase appears to contain an interesting combination of metallic bonds between transition metal and nitrogen and ionic bonds between rare-earth-like IIIB metals and nitrogen.

It is known that tantalum and niobium behave in a similar way: a comparison of the Ta–N system (*2, 3*) with the Nb–N system (*3, 4*) reveals that there are close structural parallels between tantalum nitride phases and niobium nitride phases.

At nitrogen-rich compositions fcc high-temperature phases δ-NbN$_{1-x}$ (*5*) and δ-TaN$_{1-x}$ (*2*) as well as the isostructural hexagonal phases η-NbN and η-TaN (*6*) exist. ε-TaN (*7*), on the other hand, has no counterpart in the Nb–N system. This phase exhibits a structure close to the CoSn-type structure in which the structural elements

appear to be quadratic T$_5$N pyramids. In niobium nitride phases however the T$_6$N octahedral elements are more stable than the T$_5$N structural elements. Intermediate in stability between the T$_5$N pyramids in ε-TaN and the T$_6$N octahedra in δ-NbN are the T$_6$N trigonal prismatic structural elements as observed in δ-TaN (*8*). This feature is reflected in the sequence of phases in the Ta–Nb–N system (*6*).

In view of these structural similarities and differences it appeared to be of interest to look for a ternary phase—whether isostructural with ScTaN$_{1-x}$ or not—in the Sc–Nb–N system.

2. Experimental

Two sets of experiments were performed. The first set comprised the equilibration of powder compacts of ScN and Nb at various temperatures up to 1770 K under various nitrogen pressures (1–100 kPa) and

under argon. The second set featured the nitridation of the Sc–Nb alloys (50 and 40 at.% Nb, respectively, prepared by arc-melting) in nitrogen atmosphere under the same pressures and temperatures as used for the first set. The nitridation of the Sc–Nb alloys was discontinued before the reaction was complete in order to obtain diffusion layers across the alloy samples. The sequence of the diffusion layers should reflect the various two-phase equilibria within the ternary system at different nitrogen activities. Several of these samples were reannealed in argon for homogenization of the nitrogen content obtained during the initial run. Both the metals Sc and Nb metal had a metal purity—according to the supplier—of better than 99.99%, so that any influence by Ta can be ruled out. The purity of the nitrogen was better than 99.999%. Zr foil getters were used in order to remove any residual traces of oxygen or water vapor.

The reaction products were investigated by metallography and/or by X-ray diffrac-tion of the compact materials as well as of powdered specimens.

3. Experimental Results and Discussion

No ternary phase could be observed under any of the conditions described if ScN/Nb powder compacts were used as starting mixtures. Only NbN + ScN, Nb$_2$N + ScN, or Nb + ScN could be identified by X-ray analysis. In contrast, in nitrided Sc–Nb alloys a ternary Sc–Nb–N phase could be observed. A diffractogram obtained from a compact as-nitrided sample is shown in Fig. 1. Besides the peaks of δ-NbN and ScN several lines from an additional phase can be seen. The existence of the new phases could also be confirmed in metallographic microsections. In addition to a gray-blue phase δ-(Nb,Sc)N (see below) and the well-known binary phases ScN (blue, lusterless) and δ-NbN$_{1-x}$ (metallic with a light yellow tinge) a golden yellow phase with a metallic luster could also be observed in microstructures of the nitrided Sc–Nb alloys. Ap-
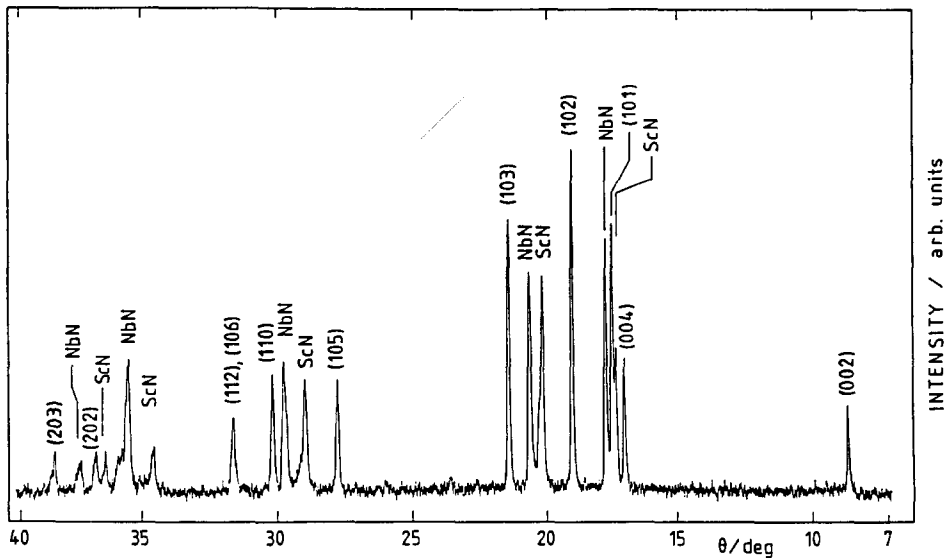

FIG. 1. X-ray powder diffractogram (Ni-filtered Cu radiation) from a diffusion layer of a nitrided NbSc alloy. Besides those of cubic δ-(Nb,Sc)N and ScN the lines of ScNbN (indexed) can be seen.

parently, ScNbN has the same color as ScTaN.

An interesting phenomenon was observed in both the powder and the compact samples of the Sc–Nb–N system and also—not previously (1) described—in samples of the Sc–Ta–N system: the fcc high-temperature phases δ-TaN and δ-NbN can apparently be stabilized by incorporation of Sc which leads to the formation of mixed ternary nitrides δ-(Ta,Sc)N and δ-(Nb,Sc)N. These phases have a gray-blue color. The lattice parameters are as follows:

δ-(Nb,Sc)N: 0.43986(8); pure $NbN_{0.86}$–$NbN_{1.00}$: 0.43820–0.43920 nm (5)

δ-(Ta,Sc)N: 0.43685(5); pure $TaN_{0.72}$–$TaN_{1.00}$: 0.4345–0.4330 nm (2).

The stabilization effect is such that δ-(Ta,Sc)N could be observed at 1670 K and 35 kPa nitrogen pressure whereas pure δ-TaN can be obtained only at temperatures above 1900 K and nitrogen pressures exceeding 1 MPa (2). No significant changes in the lattice parameter could be observed for ScN in Sc–Nb–N and Sc–Ta–N samples, indicative of a very low solubility of Nb and Ta in ScN.

4. Structure Determination of ScNbN

It was not possible to prepare a single-phase sample of the new phase. However, only a few lines from the patterns of the coexisting phases δ-(Nb,Sc)N and ScN coincide so that no serious difficulties arose during peak identification especially in view of the obvious similarities of the powder patterns of $ScNbN_{1-x}$ and $ScTaN_{1-x}$.

The pattern of $ScNbN_{1-x}$ could be indexed on the basis of a hexagonal primitive cell with $a = 0.30633(6)$, $c = 1.05702(35)$ nm with $c/a = 3.451(3)$. Powder patterns were calculated using well established computation routines (9) and best agreement

with observed intensities could be found by assuming the following structure model:

Space group $P6_3/mmc$, No. 194

   2 Sc in 2(a),
   2 Nb in 2(d),
   4 N in 4(f), $z = \frac{1}{8}$; occupancy: 50%.

The agreement between calculated and observed intensities is quite satisfactory and the model can be used to obtain better agreement by refinement techniques which for the present investigation were not available. Due to the random occupancy of nitrogen atoms at interstitial positions in most transition metal nitrides a fourfold point position for nitrogen was assumed, with a random occupancy of 50%. Due to the small scattering power of nitrogen neither the z-parameter (fixed at 0.125 here) could be refined nor any indication for a lower symmetric space group (like $P6_3mc$, with a possible twofold point position for nitrogen) could be observed.

The observed and the calculated powder patterns are listed in Table I. The diffraction lines of the coexisting phases ScN and δ-(Nb,Sc)N have not been listed but can be seen in Fig. 1. ScNbN has a longer a- and shorter c-axis than the compound ScTaN and thus the c/a ratio is shifted slightly toward the ideal value for a stacking sequence of spheres with identical diameters. The interatomic distances, based on a z-parameter of 0.125 for the nitrogen atoms are listed in Table II.

The structure of ScNbN consists of a metal layer stacking sequence of ABAC, ABAC, . . . or in the Jagodzinski-Wyckoff notation $(hc)_2$ where h indicates hexagonal and c cubic stacked layers. If the structure is discussed in terms of structural elements, it can be seen as composed of blocks of two face-sharing Sc_3Nb_3 octahedra which in turn share edges. An occupancy of 50% of the interstitial octahedral sites by nitrogen was assumed since the rule of Parthé-Yvon (10) excludes a simultaneous occupation of

			$10^4 \sin^2 \Theta$			
h k l	Θ_{obs}	d_{obs}	Observed	Calculated	I_{obs}	I_{cal}
0 0 2	8.41	5.267	213.9	212.4	27	35
1 0 0	16.87	—	—	843.1	—	<1
0 0 4	16.97	2.639	851.9	849.7	40	42
1 0 1	17.43	2.572	897.2	896.2	83, C	80
1 0 2	18.96	2.371	1055.7	1055.5	100	100
1 0 3	21.32	2.119	1321.9	1321.0	82	67
1 0 4	—	—	—	1692.7	—	≪1
0 0 6	25.95	1.760	1914.8	1911.8	1	2
1 0 5	27.76	1.654	2169.4	2170.7	30	29
1 1 0	30.20	1.531	2530.3	2529.2	33	32
1 1 2	31.58	1.471	2742.5	2741.6	6 ⎫ C	7
1 0 6	31.66	1.468	2755.0	2754.4	22 ⎭	20
2 0 0	—	—	—	3372.7	—	≪1
1 1 4	35.54	1.325	3378.8	3378.8	25, C	28
0 0 8 ⎱	35.77	1.318	3416.8	⎰3398.7⎱	15, C	⎰ 6
2 0 1 ⎰				⎱3425.3⎰		⎱ 10
1 0 7	35.95	1.312	3446.6	3445.2	11, C	10
2 0 2	36.75	1.287	3579.9	3584.6	14	13
2 0 3	38.34	1.242	3848.1	3850.2	11	11
1 0 8	—	—	—	4241.7	—	≪1
1 1 6	41.76	1.157	4435.7	4440.9	4	3
2 0 5	43.26	1.124	4696.5	4699.8	12	8
1 0 9	45.82	1.074	5143.1	5144.5	6	6
2 0 6	46.60	1.060	5279.1	5284.0	6	7

Note. I_{obs}, peak height intensity; C, coincidence.

the centers of two face-sharing octahedra (the crystallochemical reason for this phenomenon is not yet known). The result therefore is a composition ratio of ½ for nonmetal to metal.

5. Structural Relationships

In Fig. 2 the crystal structure of ScNbN$_{1-x}$ together with the structures of related compounds are shown. ScNbN is isostructural with ScTaN (*1*) and Ta$_3$MnN$_4$ (*11*). All of these compounds crystallize in an anti-TiAs-type structure (Ti in 4(f) and As in 2(a), 2(d)) which can be fairly frequently observed for transition metal pnictides (e.g., TiP) (*12*). Alternatively, ScNbN can be described as a (partially) filled La-(Nd)-type structure. It is uncertain whether

the compound Ta$_3$MnN$_4$ (*11*) actually has the stated composition with a full occupancy of interstitial sites, since it would violate the Parthé-Yvon rule.

A weaker structural similarity exists between ScNbN and a large family of carbides and nitrides, the so-called H-phases (*13*), which crystallize in the same space group as ScNbN but with a different distribution of the metal and nonmetal atoms on the same point positions. In the case of Ti$_2$AlN the Al atoms occupy the 2(d), nitrogen the 2(a), and Ti the 4(f) sites. The Ti atoms form nearly ideal octahedra around the N atoms. These octahedra are linked to each other by common corners so that it is easier to regard the Ti$_2$AlN-type structure as being based on those isolated Ti octahedra rather than on mixed Al–N octahedra.

It is very interesting to note that not only the η-NbN phase (*14*) but also a η-TaN phase (*6*) has been described as an anti-type structure as compared to ScNbN. In these phases the metal atoms occupy the 4(f) sites and thus are stacked AABB, AABB, ... The point positions of the nitrogen atoms have been given differently, either 2(a) and 2(b) (*14*) or 2(a) and 2(d) (*15*). Neutron diffraction measurements could probably clarify this discrepancy. The high-temperature γ'-Mo$_3$C$_2$ phase as well as a molybdenum nitride phase has been observed with structures similar to that of ScNbN. γ'-Mo$_3$C$_2$ (*16*) is isostructural with η-NbN and η-TaN (if the N atoms occupy the 2(d) positions), and in Mo$_{0.80}$N (*17*) the Mo atoms occupy the 4(f) sites and the N

TABLE II

INTERATOMIC DISTANCES FOR
ScNbN$_{1-x}$ (N: $z = 0.125$)

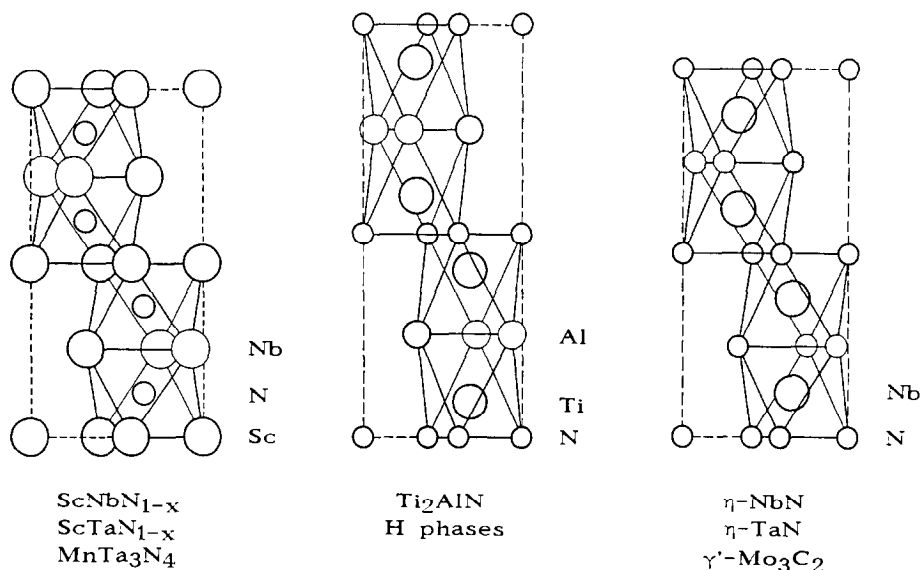| Atoms	Distance (nm)
Sc–Sc, Nb–Nb	0.3063
Sc–Nb	0.3180
Sc–N, Nb–N	0.2208

FIG. 2. Crystal structures of ScNbN as well as of isostructural and related nitrides and carbides.

atoms the 2(a) and 2(c) positions. The latter results were obtained for thin films by ammonia nitridation, and it is thus not clear whether the molybdenum nitride phase is carbon stabilized due to the possible presence of methane in ammonia gas as an impurity. Since the structural work for all those phases was performed by X-ray or electron diffraction, the point positions of the metalloid atoms are still rather tentative.

It is interesting that an intermediate phase between a metallic transition metal nitride and the ionic rare-earth-like ScN has structural features very similar to those of a pure transition metal nitride. Thus it would be interesting to investigate whether the physical behavior is also governed by the transition metal and whether unexpected properties arise from this combination, such as those which are already well known for phases in the Nd–Fe–B system. The unusual bright golden-yellow metallic appearance is a first indication that NbScN has electronic properties similar to those of pure transition metal nitrides.

References

1. W. LENGAUER AND P. ETTMAYER, J. Less-Common Met. 141, 157 (1988).
2. J. GATTERER, G. DUFEK, P. ETTMAYER, AND R. KIEFFER, Monatsh. Chem. 106, 1137 (1970).
3. C. POLITIS AND G. REJMAN, Report KfK-Ext. 6/78-1, Nuclear Research Centre Karlsruhe (1979).
4. G. BRAUER AND W. KERN, Z. Anorg. Allgem. Chem. 507, 127 (1983).
5. G. BRAUER AND H. KIRNER, Z. Anorg. Allgem. Chem. 328, 34 (1964).
6. G. BRAUER AND W. KILIANI, Z. Anorg. Allgem. Chem. 452, 17 (1979).
7. A. N. CHRISTENSEN AND B. LEBECH, Acta Crystallogr. Sect. B 34, 261 (1978).
8. G. BRAUER, E. MOHR, A. NEUHAUS, AND A. SKOKAN, Monatsh. Chem. 103, 794 (1972).
9. K. YVON, W. JEITSCHKO, AND E. PARTHÉ, J. Appl. Crystallogr. 10, 73 (1977).
10. E. PARTHÉ AND K. YVON, Acta Crystallogr. Sect. B 26, 153 (1970).
11. N. SCHÖNBERG, Acta Chem. Scand. A 8, 213 (1954).
12. "Pearson's Handbook of Crystallographic Data of Intermetallic Phases, Intermetallic Compounds"

(P. Villars and L. D. Calvert, Eds.), ASM, Metals Park, OH (1986).

13. W. JEITSCHKO, H. NOWOTNY, AND F. BENE-SOVSKY, *Monatsh. Chem.* **94**, 672 (1963).

14. G. BRAUER AND J. JANDER, *Z. Anorg. Allgem. Chem.* **270**, 160 (1952).

15. N. SCHÖNBERG, *Acta Chem. Scand. A* **8**, 208 (1954).

16. K. KUO AND G. HÄGG, *Nature (London)* **170**, 245 (1952).

17. N. V. TROITSKAYA AND Z. G. PINSKER, *Crystallography USSR* **8**, 548 (1963).