



High-temperature reactive phase formation in the Nb-N system

M. Joguet^a, W. Lengauer^{a,*}, M. Bohn^b, J. Bauer^c

^aInstitute for Chemical Technology of Inorganic Materials, Vienna University of Technology, Getreidemarkt 9/161, A-1060 Vienna, Austria

^bCentre de la Microsonde de l'Ouest, IFREMER, CNRS UMR 6538, F-29280 Plouzané/Brest, France

^cLaboratoire de Chimie du Solide et Moléculaire, CNRS-UMR 6511, Université de Rennes 1, Avenue Général Leclerc, F-35042 Rennes, France

Received 27 September 1997; received in revised form 25 November 1997

Abstract

The formation of niobium nitrides was investigated in the temperature range 1400–1800°C by reaction of niobium sheet with nitrogen (1–30 bar N₂). Equilibrated samples yielded the $p-T-[N]/[Nb]$ relationship of δ -NbN_{1-x}: $[N]/[Nb]=1.585-4.148\cdot 10^{-4}\cdot T-0.05176\cdot \ln(p_{N_2})+4.984\cdot 10^{-5}\cdot T\cdot \ln(p_{N_2})$. In diffusion couples the formation of the phases δ -NbN_{1-x}, γ -Nb₄N_{3±x} and β -Nb₂N was observed. Between δ -NbN_{1-x} and γ -Nb₄N_{3±x} a concentration discontinuity was absent, which is due to the fact that γ -Nb₄N_{3±x} is not stable in the investigated temperature range but forms upon cooling. This is visible by the typical hatched microstructure at the nitrogen-poor boundary of δ -NbN_{1-x}. The c/a ratio of the tetragonal cell of γ -Nb₄N_{3±x} increases with increasing nitrogen content. The homogeneity ranges of phases were determined from the diffusion bands by wavelength-dispersive EPMA. A portion of the phase diagram is presented. The thickness ratio of the β -Nb₂N phase band vs. the δ -NbN_{1-x}/ γ -Nb₄N_{3±x} phase band was found to be dependent on the applied nitrogen pressure. This is due to the different surface concentration of nitrogen in the δ -NbN_{1-x} phase and the influence of the homogeneity range on the layer growth rate. © 1998 Elsevier Science S.A.

Keywords: Niobium nitride; Nitridation; Layer growth; Equilibrium; Nitrogen pressure

1. Introduction

Much work has been carried out to establish the phase equilibria and clarify the structural properties of the phases in the niobium–nitrogen system especially by Brauer and coworkers and others (relevant literature is given below; for a citation of references up to 1984, the reader is referred to Brauer and Kern's works [1,2]). Most of these studies have been performed on the basis of powdered samples and only a few phase equilibria studies on compact samples were reported [3–6]. Powdered samples equilibrate faster with the gas phase at the annealing temperature but do not allow metallographic techniques to be applied and bear the danger of nitrogen pick-up during cooling [7] which can lead to an overestimate of nitrogen concentration.

Brauer and Kern [1,2] have published portions of a Nb-N phase diagram in 1983 and 1984 on the basis of powder sample data. A thermodynamic modeling of the Nb-N system was recently performed [8] but only two phases— β -Nb₂N and δ -NbN_{1-x}—were considered, which does not reflect the true situation, because two further

stable phases, γ -Nb₄N_{3±x} and η -NbN, exist. In addition, the δ -NbN_{1-x} phase was considered to be stable down to 500 K which is definitely not true according to the results of Brauer and coworkers.

Recently, we have performed a high-temperature XRD study [9] which showed that in a diffusion layer the γ -Nb₄N_{3±x} phase forms below 1140°C. This study indicated that the proposed phase field δ -NbN_{1-x}+ γ -Nb₄N_{3±x} must be different than proposed by Brauer and Kern [1,2]; γ -Nb₄N_{3±x} is rather formed upon cooling of the sample material in a quasi-continuous transition [9]. A DSC study is in progress in order to elucidate this phase transition which is, however, beyond the scope of the present study.

Diffusivity data have been measured by means of layer-growth experiments similar to the present study by Musenich et al. [4] applying nitrogen pressures up to 0.15 bar and temperatures up to 1900°C.

Because of the lack of consistency in the phase equilibria data it was decided to investigate the Nb-N system by means of diffusion couples from which the phase equilibria and nitrogen diffusivities can be investigated by characterization of the grown diffusion bands. The phase equilibria in the high-temperature region are reported in this study, experiments at lower temperatures than 1400°C are still in

*Corresponding author. E mail: wl@metec3.tuwien.ac.at

progress. For a detailed analysis of the nitrogen diffusion in $\delta\text{-NbN}_{1-x}$ and $\beta\text{-Nb}_2\text{N}$ the reader is referred to [10].

2. Experimental

Niobium sheets of 0.1-, 0.3-, 1.0- and 6-mm thickness and a purity of >99.8 m% Nb were heated in nitrogen atmosphere (>99.999 vol% N_2) in a cold-wall autoclave at 1–30 bar N_2 pressure [11]. Two-color pyrometry was employed for measurement of the temperature which was recorded for the full duration of each run. The thinner sheets (0.1 and 0.3 mm) were used to obtain equilibrated samples to determine the p – T – $[\text{N}]/[\text{Nb}]$ relationship of $\delta\text{-NbN}_{1-x}$, the thicker sheets were used for nitridation experiments which yielded a diffusion layer structure of the samples.

The samples were polished, investigated by XRD ($\text{Cu-K}\alpha$ radiation, diffracted beam graphite monochromator, Si as standard, room temperature) and EPMA, the details for the latter are reported elsewhere [12].

The weight-gain of the sample during nitridation was recorded for the equilibrated samples by weighing before and after reaction. For a more accurate characterization, the nitrogen and carbon content of these was then measured by GC-Dumas gaschromatography [13] and the oxygen content of a few samples by vacuum hot-extraction. The small carbon content of the samples stems from the starting material as well as from a small pick up during annealing. This amount does not perceptibly influence the properties of the niobium nitrides.

3. Results and discussion

3.1. The equilibrium $\delta\text{-NbN}_{1-x} + \text{N}_2$

At moderate higher-than-ambient nitrogen pressures, equilibria data of $\delta\text{-NbN}_{1-x}$ were not available in the literature. Brauer and Kern [1,2] investigated the pressure range up to 1 bar and Brauer and Kirner [14] made only a single experiment at 21 atm ($T=1300^\circ\text{C}$), the other annealings at 57–160 atm and in the range of $T=1300$ – 1500°C . Therefore, a series of equilibrium experiments was performed to establish the pressure–temperature–composition relationship in the range of 1–30 bar N_2 and 1400–1800°C. The results are given in Fig. 1 Table 1, the following formula was obtained by data fitting:

$$[\text{N}]/[\text{Nb}] = 1.585 - 4.148 \cdot 10^{-4} \cdot T - 0.05176 \ln(p_{\text{N}_2}) + 4.984 \cdot 10^{-5} \cdot T \cdot \ln(p_{\text{N}_2})$$

where p_{N_2} is the nitrogen pressure in bar, T the absolute temperature and $[\text{N}]/[\text{Nb}]$ the molar ratio of nitrogen and niobium in $\delta\text{-NbN}_{1-x}$.

The samples lower than $[\text{N}]/[\text{Nb}]=0.84$ showed split-

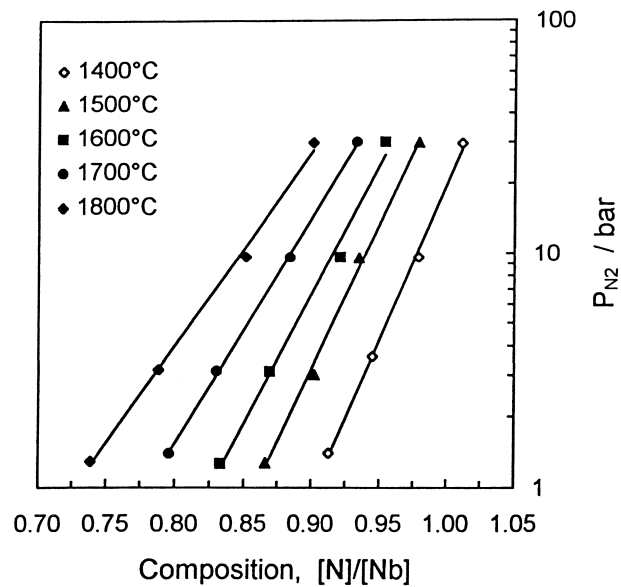


Fig. 1. Pressure–temperature–composition relationship of $\delta\text{-NbN}_{1-x}$. The samples with composition lower than $[\text{N}]/[\text{Nb}]=0.84$ transformed (partly) into $\gamma\text{-Nb}_4\text{N}_{3\pm x}$ upon cooling.

ting of the fcc diffraction lines indicative of formation of $\gamma\text{-Nb}_4\text{N}_{3\pm x}$. This formation, which cannot be avoided by quenching, hence is (almost) diffusion-less, and does not change the overall composition so that equilibrium data are not influenced.

Fig. 2 shows a plot of the c/a ratio of the transformed $\delta\text{-NbN}_{1-x}$ diffraction peaks (tetragonal transformation) for the composition region where $\gamma\text{-Nb}_4\text{N}_{3\pm x}$ formation

Table 1

Data for the p – T – $[\text{N}]/[\text{Nb}]$ relationship of the $\delta\text{-NbN}_{1-x} + \text{N}_2$ equilibrium

Sample	T K	N_2 pressure bar	Nitrogen wt%	Carbon wt%	$[\text{N}]/[\text{Nb}]$
EQ14-1	1687	1.4	11.90	0.10	0.91
EQ14-3	1673	3.6	12.18	0.12	0.93
EQ14-9	1684	9.6	12.52	0.06	0.95
EQ14-30	1675	29.7	12.98	0.14	1.00
EQ15-1	1786	1.3	11.12	0.06	0.83
EQ15-3	1776	3.0	11.80	0.10	0.90
EQ15-9	1772	9.5	12.20	0.15	0.93
EQ15-30	1785	29.9	12.62	0.08	0.96
EQ16-1	1880	1.3	10.52	0.16	0.79
EQ16-3	1872	3.1	11.07	0.29	0.85
EQ16-9	1857	9.6	12.08	0.14	0.92
EQ16-30	1865	30.0	12.39	0.07	0.94
EQ17-1	1971	1.4	10.51	0.10	0.79
EQ17-3	1972	3.1	10.85	0.20	0.82
EQ17-9	1971	9.6	11.55	0.10	0.87
EQ17-30	1977	30.1	12.13	0.08	0.92
EQ18-1	2079	1.3	9.72	0.13	0.73
EQ18-3	2073	3.2	10.24	0.41	0.79
EQ18-9	2073	9.6	11.24	0.11	0.85
EQ18-30	2076	29.9	11.77	0.09	0.89

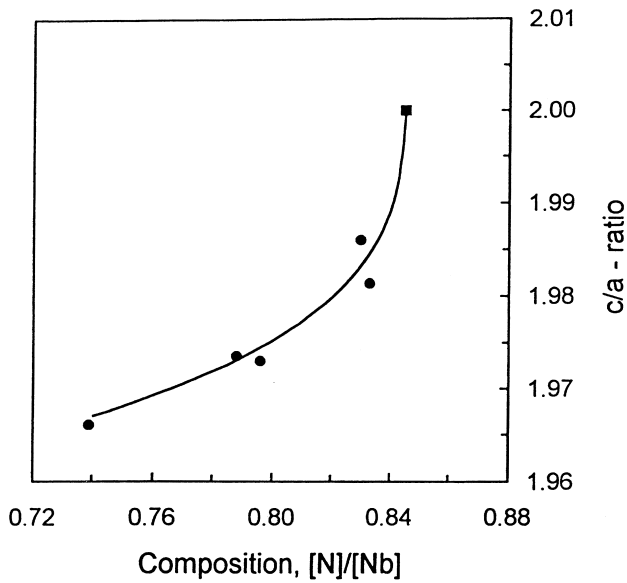


Fig. 2. c/a ratio of the tetragonal cell of $\gamma\text{-Nb}_4\text{N}_{3\pm x}$ (circles) as a function of composition. At $c/a=2$ the cell takes on the fcc structure of $\delta\text{-NbN}_{1-x}$ (square).

occurred. The splitting continuously increases with decreasing composition. When the structure has reached the fcc structure, the c/a ratio is 2 (the tetragonal $\gamma\text{-Nb}_4\text{N}_{3\pm x}$ cell is described by a structure where the c axis has almost twice the length of the fcc cell of $\delta\text{-NbN}_{1-x}$).

In Fig. 3, the perfect agreement of lattice parameters of $\delta\text{-NbN}_{1-x}$ with the values of Brauer and Kirner [14] are given.

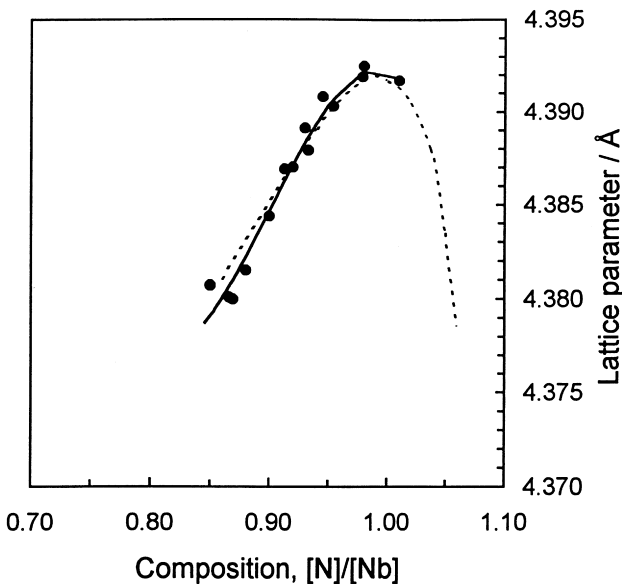


Fig. 3. Lattice parameters of $\delta\text{-NbN}_{1-x}$ as a function of composition showing perfect agreement with the data from Brauer and Kirner [14] ---. Circles and full line: present investigation.

3.2. Layer morphology, growth and composition

In the investigated temperature range (1400–1800°C) two layers, $\delta\text{-NbN}_{1-x}$ and $\beta\text{-Nb}_2\text{N}$, formed. At the nitrogen-poor side of $\delta\text{-NbN}_{1-x}$ the $\gamma\text{-Nb}_4\text{N}_{3\pm x}$ phase formed upon cooling, which can be observed from the typical hatched transformation structure (Fig. 4). The absence of a clear interface between $\delta\text{-NbN}_{1-x}$ and $\gamma\text{-Nb}_4\text{N}_{3\pm x}$ means that there is no coexistence region between the two phases at the investigation temperature, the $\gamma\text{-Nb}_4\text{N}_{3\pm x}$ is more-over formed at much lower temperatures.

The thickness ratio of the phase bands of $\delta\text{-NbN}_{1-x}$ and $\beta\text{-Nb}_2\text{N}$ showed a considerable influence of nitrogen pressure, e.g. at $T=1790^\circ\text{C}$ the δ/β thickness ratio is 1.07 at 27 bar N_2 and is 0.48 at 2 bar N_2 . This is most probably due to the surface concentration of the sample as a function of nitrogen pressure (compare Fig. 1) which changes the nitrogen flux into the sample. If the nitrogen diffusivity was calculated from these layer thicknesses the true surface concentration had to be considered [10] for each experiment or the nitrogen pressure had to be adjusted by using the results represented by Eq. 1 so as to keep the surface concentration constant at $[\text{Nb}]/[\text{N}]=0.91$. This is the only concentration which can be established between 1 and 30 bar N_2 for all samples in the temperature range 1400–1800°C. The results are reported separately [10] where also computation algorithms for obtaining nitrogen diffusivities are described, which is beyond the scope of the present study.

In Fig. 5 an EPMA line scan of the nitrogen diffusion profile is shown. By comparison with the microstructure (Fig. 4) it can be seen that a concentration discontinuity between $\delta\text{-NbN}_{1-x}$ and $\gamma\text{-Nb}_4\text{N}_{3\pm x}$ is absent, consistent with a quasi diffusionless transformation $\delta\text{-NbN}_{1-x} \rightarrow \gamma\text{-Nb}_4\text{N}_{3\pm x}$ upon cooling. Such a direct indication of the

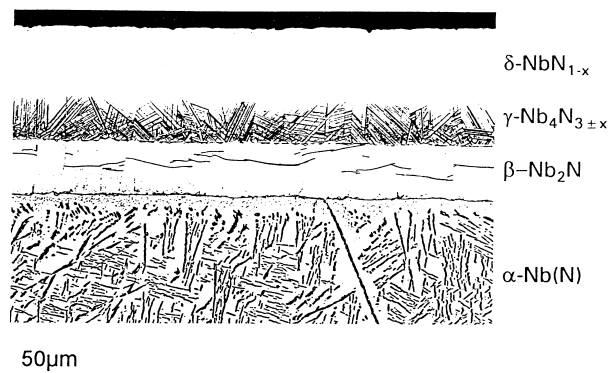


Fig. 4. Typical microstructure of the phases formed upon reaction diffusion. Top: surface in contact with nitrogen atmosphere; bottom: Nb metal. The hatched structure is caused by the transformation of $\delta\text{-NbN}_{1-x}$ into $\gamma\text{-Nb}_4\text{N}_{3\pm x}$ upon cooling. The thickness ratio $\delta\text{-NbN}_{1-x}$ (including $\gamma\text{-Nb}_4\text{N}_{3\pm x}$)/ $\beta\text{-Nb}_2\text{N}$ is dependent on the applied nitrogen pressure. Within $\alpha\text{-Nb(N)}$ the precipitation of $\beta\text{-Nb}_2\text{N}$ occurs (scattered data points).

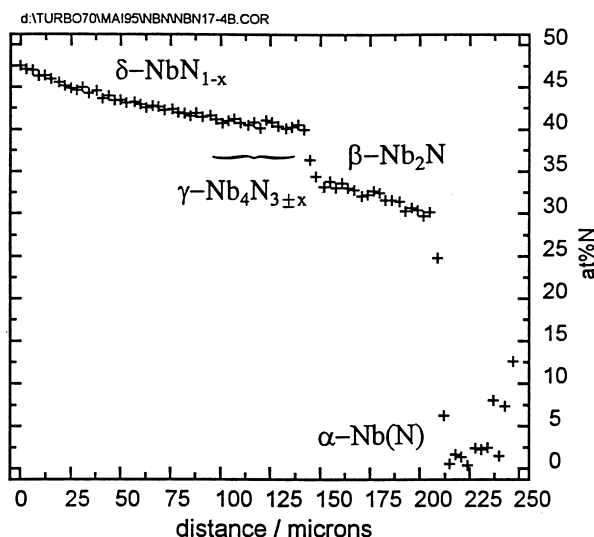


Fig. 5. EPMA nitrogen line scan perpendicular to the phase bands (compare Fig. 4).

nature of $\gamma\text{-Nb}_4\text{N}_{3\pm x}$ formation is of course not possible with powder samples and has obviously lead to wrong phase diagram information [1,2,6].

The homogeneity ranges obtained from these line scans were introduced together with the equilibria data into a portion of the Nb-N phase diagram (Eq. 1) which is shown in Fig. 6. The low-temperature region of this phase diagram is still under investigation (the temperature interval $\approx 1050\text{--}1220^\circ\text{C}$ was measured by DSC, but the two-phase field $\gamma\text{-Nb}_4\text{N}_{3\pm x} + \delta\text{-NbN}_{1-x}$ is questionable).

4. Conclusion

High-temperature nitridation experiments were employed to investigate layer growth as well as homogeneity ranges of phases in a portion of the Nb-N system. Care must be taken for the nitrogen pressure since layer growth data are influenced by the applied nitrogen pressure. The $\delta\text{-NbN}_{1-x} \rightarrow \gamma\text{-Nb}_4\text{N}_{3\pm x}$ phase transition appears in the $\delta\text{-NbN}_{1-x}$ layer in the form of a hatched region and no interphase boundary in the microstructure nor a discontinuity in the nitrogen profile is observed consistent with HTXRD results [9]. This shows that compact sample material in conjunction with metallography (and EPMA) can yield the nature of phase reactions very directly, whereas by using powder samples the occurrence of the $\gamma\text{-Nb}_4\text{N}_{3\pm x}$ phase was misinterpreted in the past.

Acknowledgements

This project was supported by the Austrian National Science Foundation, Project No. P8487-PHY. The technical assistance of DI. K. Aigner and Mr. W. Prohaska is gratefully acknowledged.

References

- [1] G. Brauer, W. Kern, Z. Anorg. Allg. Chem. 507 (1983) 127.
- [2] G. Brauer, W. Kern, Z. Anorg. Allg. Chem. 512 (1984) 7.

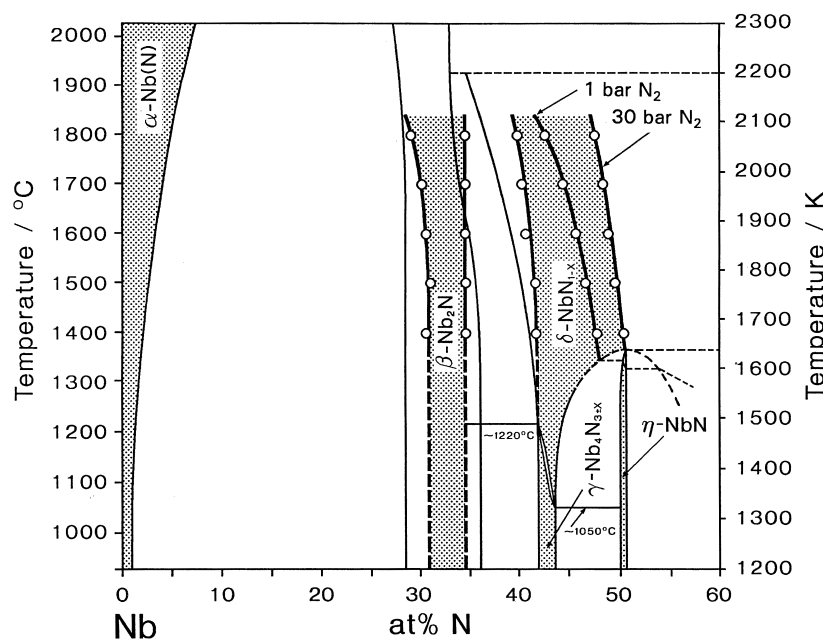


Fig. 6. Partial Nb-N phase diagram with phase boundaries measured in the present study (thick lines). Two isobars (1 and 30 bar N_2) from the equilibrium annealings were also introduced. The temperature region $\leq 1400^\circ\text{C}$ is still under investigation (the temperature vs. composition relationship of the $\delta\text{-NbN}_{1-x} \rightarrow \gamma\text{-Nb}_4\text{N}_{3\pm x}$ transformation was investigated by DSC, but the presence of the two-phase field is not certain [15]).

- [3] R. Guard, J. Sawage, D. Swarthout, *Trans. Metall. Soc. AIME* 239 (1967) 643.
- [4] R. Musenich, P. Fabricatore, G. Gemme et al., *J. Alloys Comp.* 209 (1994) 319.
- [5] W. Lengauer, P. Ettmayer, *Monatsh. Chem.* 117 (1986) 275.
- [6] C. Politis, Rejman, Kernforschungszentrum Karlsruhe (Germany), Report No. KfK-Ext. 6/78-1 (1978).
- [7] W. Lengauer, *J. Phys. Chem. Solids* 52 (1991) 393.
- [8] W. Huang, *Metall. Mater. Trans. A* 27A (1996) 3591.
- [9] R. Berger, W. Lengauer, P. Ettmayer, *J. Alloys Comp.* 259 (1997) L9.
- [10] D. Rafaja, H. Wiesenberger, W. Lengauer, M. Jorget, *Metall. Mater. Trans. A* (in press).
- [11] P. Ettmayer, A. Vendl, in: *Science of Hard Materials*, Plenum Publishing Corporation, New York, 1983.
- [12] W. Lengauer, J. Bauer, M. Bohn, H. Wiesenberger, P. Ettmayer, *Mikrochim. Acta* 126 (1997) 279.
- [13] R. Täubler, S. Binder, M. Groschner, W. Lengauer, P. Ettmayer, *Mikrochim. Acta I* 107 (1992) 337.
- [14] G. Brauer, H. Kirner, *Z. Anorg. Allg. Chem.* 328 (1964) 34.
- [15] L. Chen, W. Mayr, W. Lengauer, in preparation.