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Letter

The γ-$Nb_4N_{3\pm x}$ $\rightarrow$ δ-NbN_{1-x} phase transition

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Abstract

High-temperature X-ray diffractometry in a pressure-controlled high-purity nitrogen atmosphere was used to investigate the phase transition γ-$Nb_4N_{3\pm x}$$\rightarrow$$\delta$-$NbN_{1-x}$. The transition occurs at 1135±5 °C (for a sample at the nitrogen-rich phase boundary of the γ-$Nb_4N_{3\pm x}$ phase at [N]/[Nb]≈0.80) and is fully reversible. The separation of the (200) and (002) diffraction lines of γ-$Nb_4N_{3\pm x}$ smoothly decreases upon increasing temperature until the pattern becomes that of the fcc phase δ-NbN_{1-x} indicative of a quasi-continuous transformation. Nitridation/denitridation cycles at higher temperatures than the transition temperature yield the reaction β-Nb_2N+$N_2$$\rightarrow$$\delta$-$NbN_{1-x}$ without γ-$Nb_4N_{3\pm x}$ as an intermediate phase representative for the absence of a γ-$Nb_4N_{3\pm x}$+δ-NbN_{1-x} two-phase region. © 1997 Elsevier Science S.A.

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In numerous studies of the Nb–N system that have been carried out on different kinds of sample material (powders, compact samples, thin films) a tetragonal compound γ-$Nb_4N_{3\pm x}$ was observed which is structurally related to the fcc phase δ-NbN_{1-x} in such a way that an ordered arrangement of nitrogen atoms occurs accompanied by a shift of the Nb atoms away from the ideal fcc positions [1]. Concurrent with this shift is a tetragonal distortion of the fcc unit cell.

Substantial difficulties were encountered in proposing a Nb–N phase diagram consistent with all the findings especially to incorporate the phase reactions where γ-$Nb_4N_{3\pm x}$ is involved (e.g. [2,3]). The most recent experimental phase equilibria study by Brauer and Kern [3] reports a γ-$Nb_4N_{3\pm x}$+δ-NbN_{1-x} two-phase field below ca. 1370 °C whereas in a compilation of Storms [4] the γ-$Nb_4N_{3\pm x}$$\rightarrow$$\delta$-$NbN_{1-x}$ transition could be of the first order around ca. 1300 °C (γ+δ two-phase field) and of the second order (no γ+δ two-phase field) at higher temperatures (T≤ca. 1550 °C). δ-NbN_{1-x} appears to be stable at temperatures above 1370 °C and can be retained by quenching [5] with preparations having nitrogen contents exceeding [N]/[Nb]≈0.80. Almost all experiments on niobium nitride samples were usually performed by investigation of quenched material at room temperature. If, however, the phase transition between γ-$Nb_4N_{3\pm x}$ and δ-NbN_{1-x} is indeed a diffusionless (martensitic) or a very fast transformation involving nitrogen diffusion only over small distances, then quenching experiments have to be suspected to be inappropriate to yield a consistent picture of the phase equilibria at high temperatures. Thus, for phase equilibria investigation, high-temperature X-ray diffraction (HTXRD) can be an appropriate method for an in situ investigation. Two HTXRD studies were indeed already reported in the literature concerning the γ-$Nb_4N_{3\pm x}$$\rightarrow$$\delta$-$NbN_{1-x}$ transformation. Kim and Franzen [6] have used a HTXRD chamber to prepare γ-$Nb_4N_{3\pm x}$. However, they did not comment on their results with respect to the transformation temperature but rather on the application of the Landau theory on the structural links between γ-$Nb_4N_{3\pm x}$ and δ-NbN_{1-x}.

In the work of Christensen [7] an attempt was made to find the $\gamma$$\rightarrow$$\delta$ transition temperature. Lattice parameters of β-Nb_2N, γ-$Nb_4N_{3\pm x}$ and δ-NbN_{1-x} as a function of temperature were reported which indicate that the transition should occur between ca. 1550 and 1663 °C. Any further experimental details such as the nitrogen pressure in the HTXRD chamber were not given. The nitrogen pressure, however, is of crucial importance since niobium nitrides have quite a high nitrogen equilibrium pressure

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which has to be maintained during HTXRD work—at least at T>ca. 1200 °C where the nitrogen diffusivities [12] in niobium nitrides become significant (e.g. at 1700 °C and 1 bar N_2 the δ-NbN_{1-x} layer formed on niobium metal has a thickness of ca. 100 μm after an annealing time of 3 h).

In order to be able to observe the phase transformations in the composition region between β-Nb_2N and δ-NbN_{1-x} under equilibrium conditions a HTXRD chamber (HTK-10, A. Paar KG, Austria) was used which was mounted on a Philips diffractometer. The device was modified in such a way that the original X-ray window (consisting of Kapton® foil) was exchanged against a Ni foil of a thickness such that it also served as a filter for the Cu radiation. This procedure guarantees high-purity conditions by avoiding oxygen diffusion through the window. The nitrogen atmosphere (>99.999 vol% N_2, AGA, Austria) was additionally purified over activated copper (Oxisorb®, Messer-Griesheim, Germany) mounted in the N_2 supply line as well by Ti and Zr getters heated inside the chamber. A 140×10×1 mm Nb metal strip (>99.9 wt% Nb, Metallwerk Plansee, Austria) was placed between the water-cooled sample holders of the chamber and heated by electrical current. The use of a compact Nb strip rather than Nb powder spread onto the surface of an (inert) heating strip avoids the temperature gradient between the thermocouple and the sample that is usually encountered in HTXRD of powdered material. For temperature measurement and control a Pt 10% Rh thermocouple was tightly squeezed into a borehole of the heating strip. In addition, a hot-filament pyrometer was used for temperature measurement. Heating/cooling was automatically controlled by the HTK-2 temperature controller of the chamber which was connected to a PC for XRD and temperature control and data acquisition [8]. The nitrogen pressure was adjusted via a capillary gas inlet and measured with a piezoelectric gauge. The diffractograms were recorded in steps of 2Θ= 0.02° with a counting time of 1–2 s.

After a careful re-investigation [9] of the temperature–pressure composition relationship of δ-NbN_{1-x} (on the basis of compact samples in order to avoid compositional shifts by nitrogen pick-up during cooling) appropriate nitrogen pressures could be adjusted.

Fig. 1 gives the results of a HTXRD experiment with a constant temperature of 1330 °C and varying nitrogen pressures. The reversible reaction β-$Nb_2N+N_2 \rightarrow \delta$-$NbN_{1-x}$ obviously occurs between 4 and 10 mbar N_2, which is higher than the work of Brauer and Kern [3] implies for the β-Nb_2N/δ-NbN_{1-x}/N_2 equilibrium at this temperature (they actually supposed that γ-$Nb_4N_{3\pm x}$ was involved in this equilibrium). Similar experiments were performed at other temperatures in the range 1200–1400 °C with the same result, i.e. the absence of γ-$Nb_4N_{3\pm x}$.

Corresponding results were obtained from diffusion couples (see below and [11]) in the temperature range 1200–1800 °C (some of them were performed in a temperature gradient so as to obtain a smooth variation of temperature), where the same type of microstructure was obtained, i.e. the absence of an interface between δ-NbN_{1-x} and γ-$Nb_4N_{3\pm x}$, the presence of which would be due to a two-phase field δ-$NbN_{1-x}+\gamma$-$Nb_4N_{3\pm x}$. These experiments are proof that the two-phase field γ-$Nb_4N_{3\pm x}+\delta$-NbN_{1-x} does not exist at $T \geq 1200$ °C.

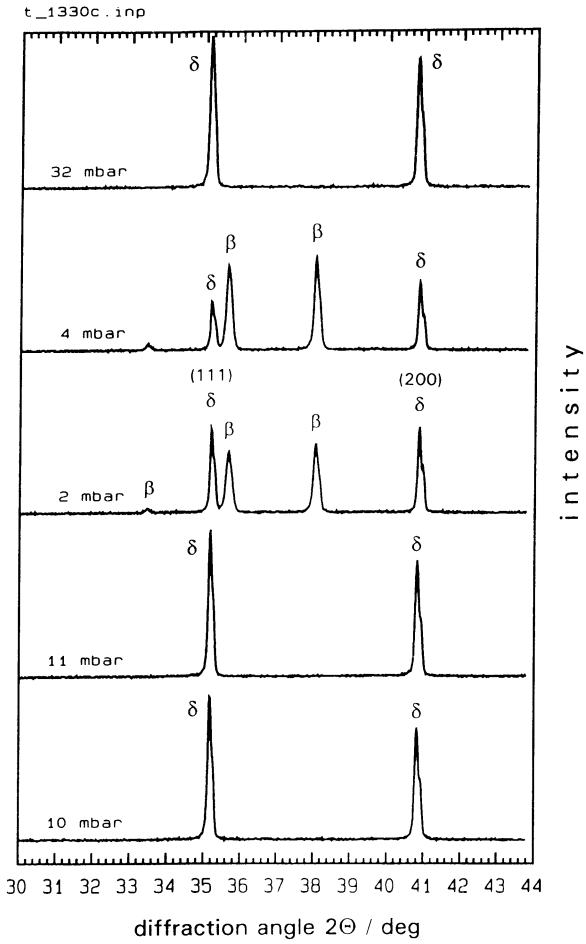

Fig. 1. X-ray diffractograms at 1330 °C where the (diffusion-controlled) phase reaction β-$Nb_2N+N_2 \rightarrow \delta$-$NbN_{1-x}$ could be observed as a function of nitrogen pressure (given on the left). At 10, 11 and 32 mbar N_2 the sample is single phase δ-NbN_{1-x} and at 2 and 4 mbar N_2 it is two-phase δ-$NbN_{1-x}+\beta$-Nb_2N. The shoulder on the right of the (200) line is due to $K\alpha1/K\alpha2$ splitting. No tetragonal splitting of the (200) line could be observed. The layer growth of η-NbN is too slow to be observed within the reaction time. The total intensity of the y axis is 20 000 counts s^{-1}. The diffraction angle was corrected for the goniometer offset.

In these experiments the η-NbN phase—which should be stable up to 1370 °C—did not form even after 3.8 h reaction time and even if the pressure was increased to just below ambient pressure because of the low growth rate.

In Fig. 2 a continuation of the HTXRD experiment of Fig. 1 is shown with heating/cooling cycles. At room temperature clearly separated (200) and (002) diffraction

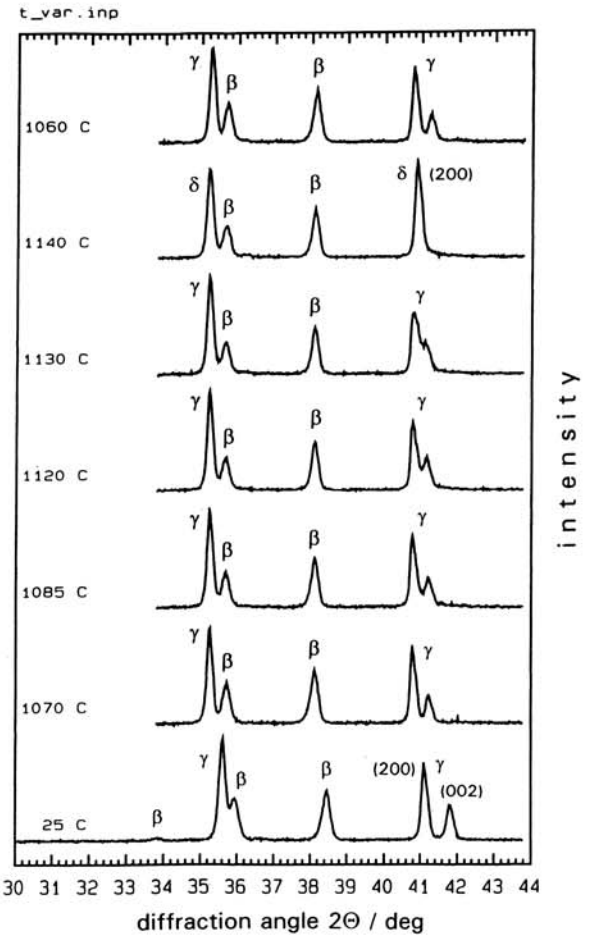

Fig. 2. X-ray diffractograms at various temperatures (given on the left) and a nitrogen pressure of 0.5 mbar (time sequence of recording: from bottom to top). The appearance of the cubic (200) line from the tetragonal lines (200) and (002) could be observed between 1130 and 1140 °C indicative of the transition γ-$Nb_4N_{3\pm x}$→δ-NbN_{1-x}. This transition is reversible. The overall shift of the peaks is due to the thermal expansion of the sample. The diffraction angle was corrected for the goniometer offset. The intensity of the total y axis is 20 000 counts s^{-1}.

lines of the γ-$Nb_4N_{3\pm x}$ phase could be observed. Upon stepwise increasing the temperature (the nitrogen pressure in the heating chamber was at 0.5 mbar) the separation becomes continuously smaller until at 1140 °C the pattern becomes cubic. Thus the transformation temperature γ-$Nb_4N_{3\pm x}$→δ-NbN_{1-x} is between 1130 and 1140 °C. This temperature is so low that a control of the N_2 pressure was not necessary if the HTXRD experiments took less than a few hours, because the nitrogen diffusivity in this temperature region is very low. Because the transformation is very fast only short diffusion paths seem to exist to transform one structure into the other (quasi-continuous transition). The smooth decrease of tetragonality upon increasing temperature is indicative of this quasi-continuous transition in which the c/a ratio of the tetragonal cell smoothly

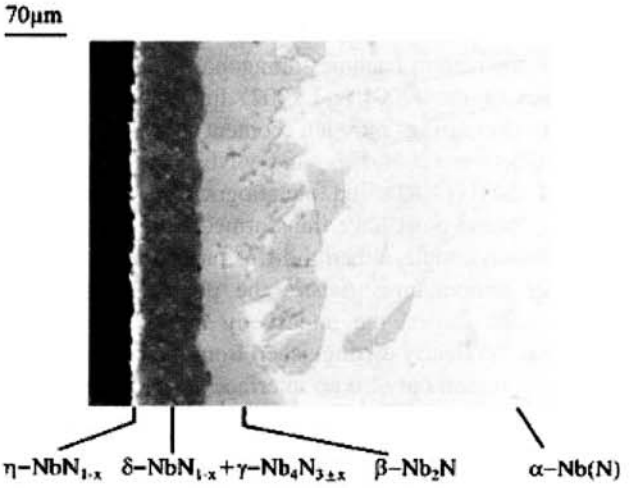

Fig. 3. Microstructure of a Nb/N_2 diffusion couple annealed for 330 h at 1200 °C. The phase band sequence β-Nb_2N/γ-$Nb_4N_{3\pm x}$+δ-NbN_{1-x}/η-NbN_{1-x} onto the Nb core were observed (EPMA: Fig. 4; XRD: Fig. 5). The tilt angle of polishing for enlargement of the phase bands was 30°, anodically oxidized.

approaches 2, which means that the fcc structure is attained (the c-axis of the γ-$Nb_4N_{3\pm x}$ cell is slightly smaller than twice the fcc cell parameter).

Because of the relatively high nitrogen pressure the transformation temperature applies to the nitrogen-rich boundary of γ-$Nb_4N_{3\pm x}$ which is located near 45 at% N ($NbN_{0.81}$). This value applies to a temperature of 1200 °C at which a Nb/N_2 diffusion couple was prepared (Fig. 3) and investigated with EPMA (Fig. 4). In this diffusion couple XRD (performed with intermediate stepwise re-

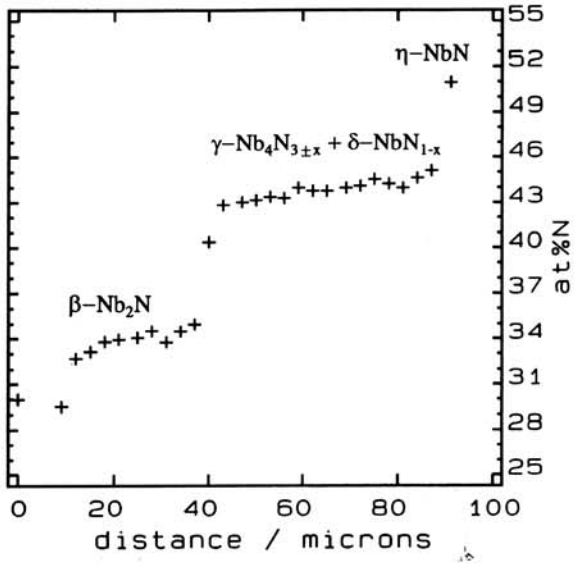

Fig. 4. EPMA nitrogen line scan on a Nb/N_2 the diffusion couple [10] shown in Fig. 3 showing the compositional range of the γ-$Nb_4N_{3\pm x}$+δ-NbN_{1-x} phase band.

moval of layers by etching [11]) showed that the outermost part of the 'δ-NbN_{1-x}+γ-$Nb_4N_{3\pm x}$' layer is δ-NbN_{1-x}, and then the pattern becomes tetragonal with an increasing separation of the (200) and (002) lines upon increasing depth (=decreasing nitrogen content); see Fig. 5. No interface between δ-NbN_{1-x} and γ-$Nb_4N_{3\pm x}$ is present. In view of the HTXRD and metallographic results the γ-$Nb_4N_{3\pm x}$ phase must have transformed from δ-NbN_{1-x} in this diffusion couple. When a diffusion couple is annealed at higher temperatures (where the phase bands can be grown much larger) the intensively hatched γ-$Nb_4N_{3\pm x}$ region can be clearly distinguished from the coarse-grained δ-NbN_{1-x} region but also no interface appears between the two phases (compare [11]). The composition range of the 'γ-$Nb_4N_{3\pm x}$+δ-NbN_{1-x}' phase band in the sample shown in Fig. 3 is 42.9–44.8 at% N ($NbN_{0.75}$–$NbN_{0.81}$) in good agreement with a study on equilibrated bulk samples where tetragonal patterns were observed at room temperature in all samples having [N]/[Nb]≤0.82 [9].

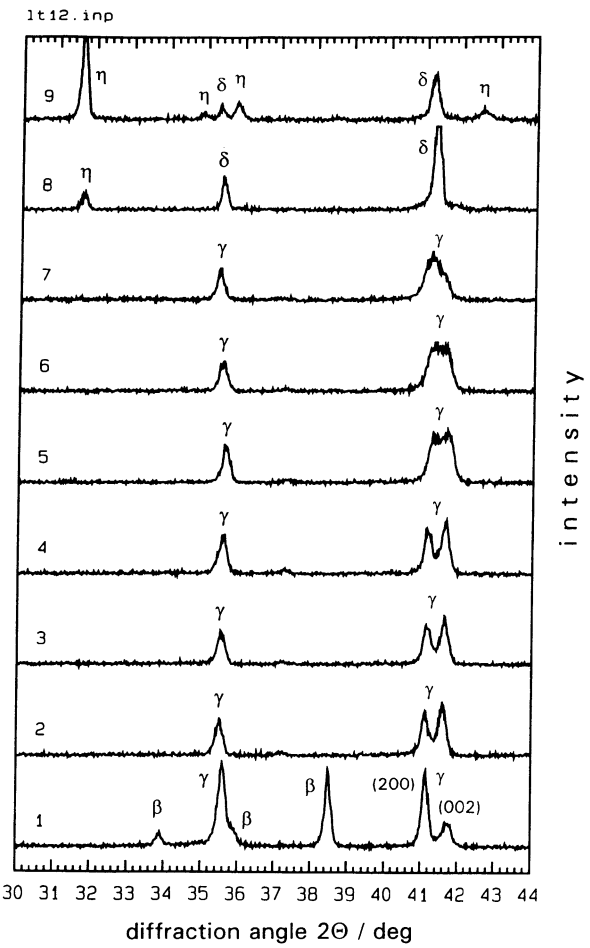

Fig. 5. XRD patterns (at room temperature) obtained by stepwise removal of layers by etching [11] the diffusion couple shown in Fig. 3. Surface: pattern #9. The thickness of removed material between pattern #9 and #2 is only about 10 μm; pattern #1 is from a powdered sample. Only the outermost part (pattern #8) of the 'δ-NbN_{1-x}+γ-$Nb_4N_{3\pm x}$' layer shows an fcc pattern, then the (200) line separates increasingly into the tetragonal lines (200) and (002). A metallographic differentiation between δ-NbN_{1-x} and γ-$Nb_4N_{3\pm x}$ is not possible because the δ-NbN_{1-x} part is too thin (compare [11]).

The findings of Christensen [7] who has reported the transition temperature between ca. 1550 and 1663 °C is in clear disagreement with our results. At the high-temperature region of Christensen's investigation the layer growth rate and nitrogen diffusivities in the solid phases are so high [9,11] that an adjustment of the nitrogen pressure in the X-ray chamber appears to be absolutely necessary (e.g. the nitrogen pressure to keep $NbN_{0.78}$ in equilibrium with the gas phase at T=1600 °C is 0.7 bar N_2). However, no experimental details and precautions or data other than lattice parameters were reported in the work of Christensen [7]. His lattice parameters of γ-$Nb_4N_{3\pm x}$ as a function of temperature as taken from a graph appear to be in favour of the hypothesis that a change in composition of the sample may have occurred during this experiment because the thermal expansion calculated from the lattice parameters gives an improbable thermal expansion coefficient of ca. 4×10^{-6} K^{-1} which is much too low (compare [5]).

Because of our present findings the knowledge of the phase relationships of γ-$Nb_4N_{3\pm x}$ with other niobium nitride phases have to be revised. From diffusion couple studies [11] it was clear that the δ-NbN_{1-x}→γ-$Nb_4N_{3\pm x}$ phase transition cannot be suppressed by quenching. Probably a quasi-continuous transformation of second order takes place in agreement with Kim and Franzen [6] and Kim et al. [13]. In a recent thermodynamic assessment [14] only the β-Nb_2N and δ-NbN_{1-x} phases were considered. The phases γ-$Nb_4N_{3\pm x}$ and η-NbN were excluded because it was assumed that they are oxygen stabilized. In contrast, the present work, many other studies (e.g. [1–3,6,13]) and our diffusion couple studies [9,11] show that oxygen contamination can be safely excluded from being responsible for a stabilization of the latter phases and the phases can indeed be considered as binary niobium nitride phases. In view of the confusing situation with respect to phase equilibria it appears that some more experimental as well as modelling work has still to be made for establishing a Nb–N phase diagram.

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