Synthesis of cubic niobium nitride by reactive diffusion under nitrogen pressure

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ABSTRACT

The synthesis of niobium nitride by reactive diffusion in a furnace at 1395–1475 °C and under nitrogen pressure in the range 2–25 MPa was investigated. In experiments, we used compacted Nb powder with a mean particle size of 43 μm. Phase transformations in the product as studied by electron probe microanalysis (EPMA) were found to proceed in the following order: $Nb \rightarrow \alpha\text{-}Nb(N) \rightarrow \beta\text{-}Nb_2N_{1\pm x} \rightarrow \gamma\text{-}Nb_4N_{3\pm x} \rightarrow \delta\text{-}NbN_{1\pm x}$. The size of niobium particles which could react with nitrogen to yield cubic niobium nitride was estimated (SEM analysis) from the dependence of the thickness Δ of the $\delta\text{-}NbN_{1\pm x}$ outer layer formed on the surface of Nb particles on the dwell time t_{dw} at 1460–1473 °C. It was shown that Δ grew nearly proportional to t_{dw}. At t_{dw} = 30 min and $P(N_2)$ = 2 MPa, Δ was found to attain a value of about 15.5 μm. Prolonged heating ($t_{dw} \approx 60$ min) was found to result in decomposition of the single-phase cubic niobium nitride into a two-phase (multiphase) product. This was confirmed by XRD data and magnetic measurements which showed the occurrence of two different critical temperatures T_c in the same sample. The maximum critical temperature T_c was found to attain a value of 15.6 K.

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1. Introduction

Niobium nitrides are known to exist within an extended homogeneity range and their properties—such as good thermal stability [1], high microhardness [2], remarkable corrosion resistance [3], etc.—strongly depend on their composition. Among these compounds, cubic niobium nitride ($\delta\text{-}NbN_{1\pm x}$) is of especial interest as a high-T_c superconductor with T_c = 17.3 K [4–6]. Superconducting properties of this compound also are composition-sensitive.

At high-temperatures, niobium is highly reactive with respect to nitrogen gas. Three methods are generally used to prepare niobium nitrides: synthesis of niobium nitride powders by high-temperature reactive diffusion [7], synthesis of bulk samples [8], self-propagating high-temperature synthesis (SHS) of powders [9,10] and bulk samples [4], and plasmochemical synthesis of thin niobium nitride films [11]. Niobium nitride fibers can be obtained upon thermal decomposition of niobium alkoxide–cellulose gel fibers in an NH_3 atmosphere at temperatures around 1400 °C [12]. A variety of niobium nitride phases is known to exist in the Nb–N system: $\alpha\text{-}Nb(N)$ solid solution, $\beta\text{-}Nb_2N_{1\pm x}$, $\gamma\text{-}Nb_4N_{3\pm x}$, $\delta\text{-}NbN_{1\pm x}$, $\varepsilon\text{-}NbN_{1\pm x}$ [7,13,14], and also other N-rich phases such as Nb_5N_6 and Nb_4N_5 [15].

In this work, we explored the mechanism for formation of $\delta\text{-}NbN_{1\pm x}$ in conditions of reactive diffusion upon variation in process parameters and hence in the microstructure, composition, and superconductivity of resultant nitride powders.

2. Experimental

In experiments, we used the Nb powder with a mean particle size of 43 μm (325 mesh). The particle size distribution of this powder (as determined with a Laser Particle Sizer Analysette 22) and its microstructure are shown in Figs. 1 and 2, respectively.

All experiments were carried out at 1395–1475 °C in a GHC-20 Unipress high-pressure–high-temperature unit under nitrogen pressures $P(N_2)$ in the range 2–25 MPa and dwell times of 0–60 min. Pelleted niobium samples 3 mm × 4 mm × 25 mm in size (porosity 35–38%) were placed into a boron nitride crucible and then put into a one-heating-zone furnace (Fig. 3). The furnace was then accommodated inside a high-pressure chamber. Before synthesis, the samples were dried at 160 °C in vacuum (10^{-4} Pa, see Fig. 4). Then the chamber was filled with nitrogen to a required value of $P(N_2)$ and heat-treated according to the schedule shown in Fig. 4. The dwell time t_{dw} at a maximum possible temperature (1550 °C) could be varied between 0 min and several hours. Temperatures T_1, T_3, and T_4 (see Fig. 3) were measured with thermocouples.

The product of reactive diffusion was characterized by XRD. The diffraction patterns were taken with a Phillips Expert diffractometer (Cu Kα1 radiation, 2θ = 15–125°, angle pitch 0.017°, acquisition time 1024 s). According to the XRD data, a main phase of the product was cubic niobium nitride whose composition was determined in weight gain experiments. The lattice parameter of

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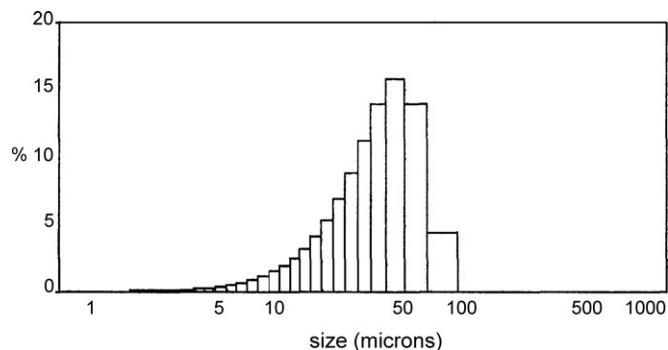E-mail address: rose-marie.ayral@univ-montp2.fr (R.-M. Marin-Ayral).

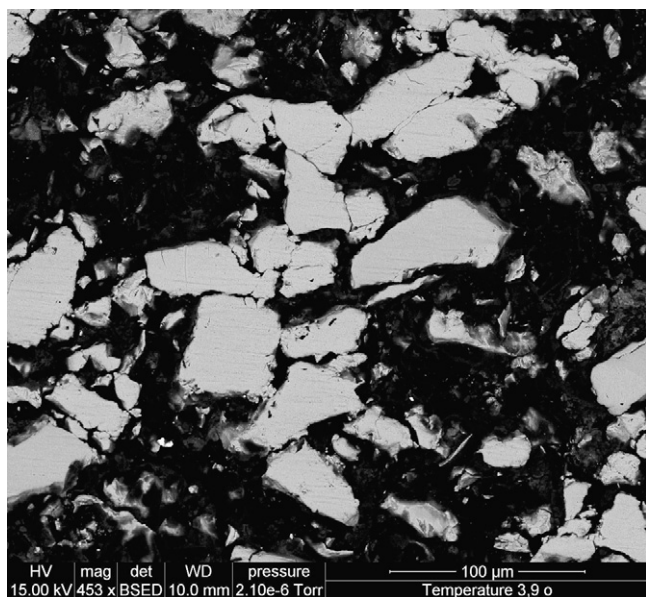**Fig. 1.** Size distribution of starting Nb powder.

Fig. 2. Microstructure of starting Nb powder.

synthesized cubic niobium nitrides was determined using the Celref software. Micrographs were taken with a Leo S260 or Hitachi 4500I SEM device. Phase formation in products was studied by electron probe microanalysis (EPMA). Magnetic susceptibility was measured with a Quantum Design MPMS-XL SQUID magnetometer. Critical temperatures T_c were measured with an accuracy of 0.1 K.
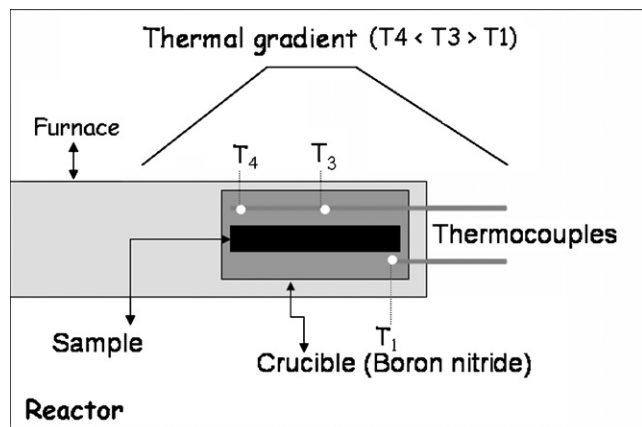

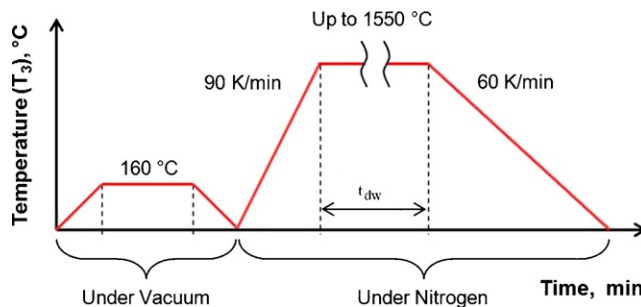**Fig. 3.** Schematic of the experimental setup.

Fig. 4. Schedule of heat treatment.

3. Results and discussion

3.1. Dependence of nitrogen content on process parameters

Fig. 5 shows the stoichiometric coefficient x (in NbN_x) as a function of dwell time t_{dw} at $T_{dw} = 1460 \pm 10$ °C and $P(N_2) = 2$ MPa. It follows that x initially grows with increasing t_{dw} and then levels-off. It is noteworthy that a value of $P(N_2) = 2$ MPa was chosen because, according to the results of weight gain measurements, in this case it was possible to obtain cubic niobium nitrides within a wide range of x and thus to investigate their properties. It was difficult for us to obtain overly stoichiometric compounds ($x > 1$) under reduced nitrogen pressures (below 2 MPa), while under higher pressure (above 2 MPa), we could not obtain products with low x.

According to the weight gain data, cubic niobium nitrides can be obtained within the wide range of x: $0.93 < x < 1.01$. However, microstructure investigation has shown that the larger particles in starting powder remained partially unreacted (for all t_{dw}). Internal layers of the samples were found to contain also γ-$Nb_4N_{3\pm x}$, β-$Nb_2N_{1\pm x}$, and unreacted Nb. At $t_{dw} = 6$ min, more or less uniformly nitrided were the particles up to 28 μm in size, while at $t_{dw} = 60$ min, the particles up to 66 μm in size. In view of this, the mechanism of phase formation in the product was investigated in experiments with coarser powders (with a particle size about 100 μm).

3.2. Microstructure

As can be inferred from the micrograph presented in Fig. 6a, phase formations during reactive diffusion proceed in the following order. First, a solid solution of nitrogen in niobium
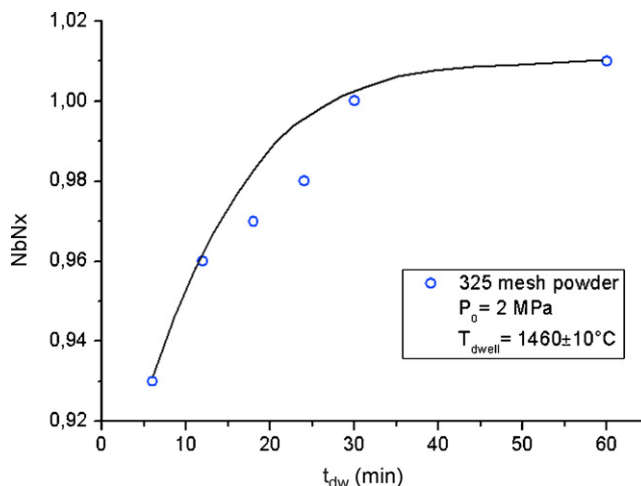

Fig. 5. Stoichiometric coefficient x in NbN_x as a function of t_{dw}: $T_{dw} = 1460 \pm 10$ °C, $P(N_2) = 2$ MPa.