JOURNAL OF MATERIALS SCIENCE 19 (1984) 2915–2920

Preparation and superconductivity of NbN powder by a vapour phase reaction

T. WATARI, Y. TAKAKURA, M. MURAKAMI, A. KATO
Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan

The formation of superconducting NbN powders by the vapour phase reaction of the $NbCl_4$–NH_3–H_2 system has been investigated. The properties of NbN powders changed with the reaction temperature, mixing temperature of $NbCl_4$ and NH_3, and gas composition ratio ($[NH_3]/[NbCl_4]$). The reaction system gave NbN powders consisting of particles with sizes less than 50 nm. The process of particle formation is discussed. The NbN powders produced had vacancies at both the Nb and N sublattices. The vacancies influenced the superconducting transition temperature (T_c) of NbN, the highest T_c observed being 14.1 K.

1. Introduction

The superconducting compounds with NaCl and A-15 type structures are superior to Nb–Ti alloys. However, their brittleness gives rise to many difficulties in the fabrication of superconducting materials. If one can produce a compositie superconductor in which the powders of the superconducting compound are dispersed in a metal matrix, it is expected that such a composite will be fairly flexible and may solve some difficulties in the application of NaCl and A-15 type compounds for superconductors. From this point of view, the present authors have investigated the preparation of fine powders of Nb_3Sn and Nb_3Ge with A-15 type structure and their superconducting properties [1–3].

On niobium nitride, which is a typical superconducting compound with NaCl structure, the films were obtained by r.f. reactive sputtering [4] and vapour phase reaction [5], but the powders were obtained only by spray drying [6]. This paper describes the preparation of NbN powders by the vapour phase reaction of the $NbCl_4$–NH_3–H_2 system and their superconducting transition temperatures.

2. Experimental procedure

The reaction was carried out by a flow method using a horizontal alumina reactor. The reactor used is illustrated in Fig. 1. Experimental details are similar to those described elsewhere [1]. The $NbCl_4$ vapour was prepared by the reaction of niobium metal and argon-carried chlorine at 900 to 950° C and mixed with an ($NH_3 + H_2$) stream at position A in Fig. 1. Because the mixing temperature (T_M) of the $NbCl_4$ vapour and ($NH_3 + H_2$) stream had a strong influence on the properties of the NbN powder, T_M was varied by shifting position A. The powders produced were collected in a flask.

The reaction conditions used were as follows: reaction temperature (T_R) = 800 to 1400° C, T_M = 650 to 1200° C, total gas flow rate = 500 to 600 $cm^3 min^{-1}$, $NbCl_4$ concentrations = 0.8 to 2.3%, NH_3 concentration = 1.5 to 16.4%, H_2 concentration = 40 to 65% (balance argon).

The overall reaction is

$$NbCl_4(g) + NH_3(g) + 1/2\,H_2(g) \rightleftharpoons NbN(s) + 4HCl(g) \qquad (1)$$

and has equilibrium constants of $10^{8.2}$ (1000° C) and $10^{8.1}$ (1400° C).

The powder products were identified by X-ray diffraction (Co$K\alpha$). The lattice constant of NbN was calculated from the (1 1 1) and (2 0 0) diffraction lines, in which silicon was used as an internal standard material. The particle shape and size were

0022–2461/84 $03.00 + .12

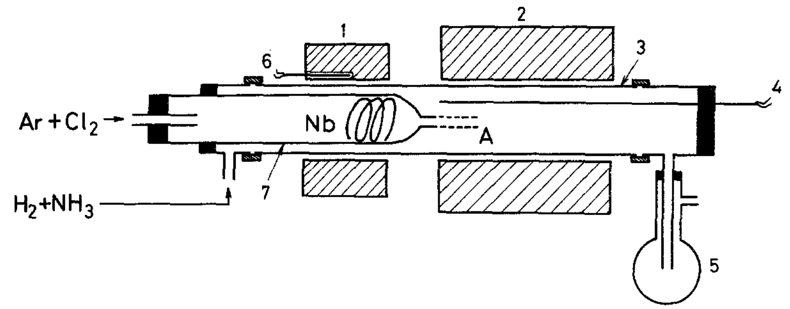

Figure 1 Reaction apparatus. 1, Kanthal heater (length 230 mm); 2, SiC resistance furnace (length 400 mm); 3, alumina tube (internal diameter 22 mm, length 1000 mm); 4, Pt/Pt–Rh (13%) thermocouple; 5, collecting flask; 6, chromel–alumel thermocouple; 7, quartz tube (internal diameter 16 mm).

observed using the transmission electron microscope. The nitrogen content of the NbN powders was determined by measuring the amount of nitrogen evolved when the powders were burned.

The samples for measuring the critical temperature (T_c) were made by mixing NbN and indium powders in the ratio of 7 to 3 in weight and forming in a compact (diameter 1.5 mm, length 15 mm). The resistance of the compact was measured by a four probe method. The sample temperature was measured with a germanium resistance thermometer.

3. Results and discussion

There are five nitride phases in the Nb–N system: β-Nb_2N, γ-Nb_4N_3, δ'-NbN, δ-NbN and ϵ-NbN [7]. δ-phase (NaCl structure) has the highest T_c among these phases. The lattice constant and T_c of the δ-phase varies with the N/Nb ratio [8, 9]. δ-NbN has the maximum lattice constant of 0.4392 nm at the N/Nb ratio of 0.99 [8] and the maximum T_c of 16.3 K at the atomic ratio of 0.95 [9].

3.1. Lattice constant of δ-NbN phase

The phases of niobium nitride powders produced in this system changed with the reaction temperature (T_R), mixing temperature (T_M), and gas composition ratio $[NH_3]/[NbCl_4]$ (X). Pure δ-phase was produced at $T_R = 800$ to 1200° C, $T_M = 800^\circ$ C and $X = 1$ to 12. At high reaction temperatures, $T_R = 1400^\circ$ C and $T_M = 800^\circ$ C, however, the other nitride phases were produced: β-phases ($X \fallingdotseq 1$), γ-phase ($X \fallingdotseq 2$) and δ-phase ($X = 2.5$ to 11). Fig. 2 shows the variation of the phases in powder products and the lattice constant (a_0) of the δ-phase with the mixing temperature. The nitride phase of the powder was pure δ-phase at $T_M \leqq 900^\circ$ C, but δ'- and β-phases appeared at $T_M \geqq 1000^\circ$ C and it became β-phase alone at $T_M = 1200^\circ$ C. The value of a_0 of the δ-phase was constant at $T_M \leqq 800^\circ$ C and decreased with the increase of T_M above 900° C.

Fig. 3 shows the dependences of the lattice constant and the N/Nb ratio of the δ-phase on the reaction temperature. Fig. 4 shows the dependence of the lattice constant of δ-NbN on the ratio $[NH_3]/[NbCl_4]$. As seen in Fig. 4, the ratio N/Nb increased with the increase of X at every reaction temperature, but the dependence of a_0 on X varied with reaction temperature, indicating that the defect structure of the δ-phase changed in a complicated manner with the reaction temperature.

The relation between the lattice constant and the N/Nb ratio of the δ-phase is summarized in Fig. 5. The δ-phase had the maximum lattice constant at the ratio N/Nb of 0.9. The present result differs from that of G. Brauer *et al.* (dashed

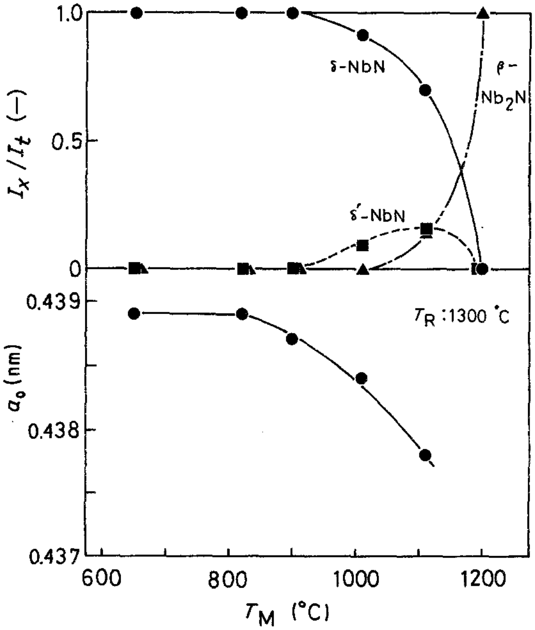

Figure 2 Variation of phase composition in powder products and lattice constant of δ-NbN phase with mixing temperature. I_x: δ-NbN, $I_{(111)}$; δ'-NbN, $I_{(101)}$; β-Nb_2N, $I_{(101)}$. $I_t = I_{\delta\text{-NbN}} + I_{\delta'\text{-NbN}} + I_{\beta\text{-}Nb_2N}$. $[NH_3] = 5.5\%$, $[NbCl_4] = 1.5$ to 1.6%, $[H_2] = 48\%$ (balance Ar).

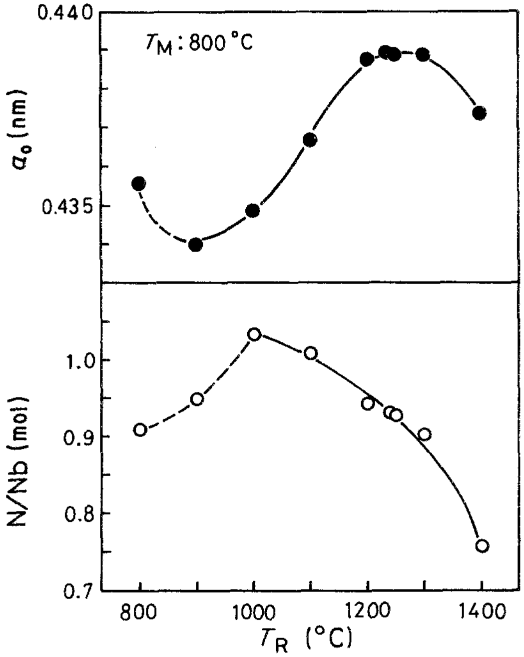

Figure 3 Dependences of lattice constant and atomic ratio N/Nb of δ-NbN phase on reaction temperature. $[NH_3] = 5.5\%$, $[NbCl_4] = 1.4$ to 1.5%, $[H_2] = 47\%$ (balance Ar).

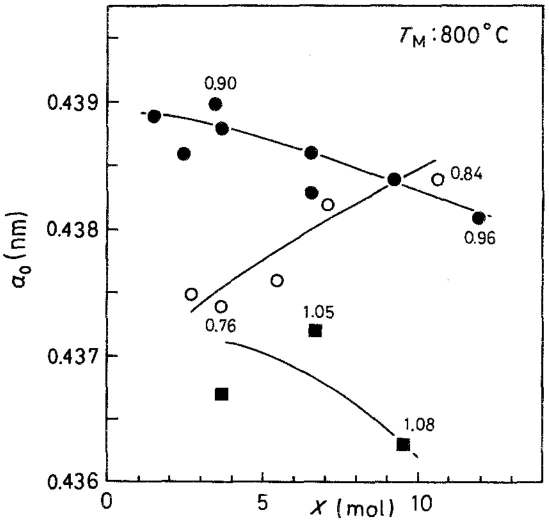

Figure 4 Dependence of lattice constant of δ-NbN phase on the ratio $[NH_3]/[NbCl_4]$ in the reacting mixture. Numerals indicate N/Nb ratio. $[NH_3] = 1.9$ to 16.4%, $[NbCl_4] = 0.8$ to 2.3%, $[H_2] = 42$ to 65% (balance Ar). T_R: ■, 1100° C; ●, 1200° C; ○, 1400° C.

line) [8]. This may be due to the difference of the preparation methods. In [7], δ-NbN was prepared by nitridation of niobium metal at 1200 to 1500° C and 160 atm. Otherwise, it is presumed that NbN powders produced by the present method, owing to the rapid formation and the short heating time of NbN particles, may include more vacancies than those produced under an equilibrium state. J. Hojo *et al.* [10] reported that the vanadium and titanium nitride powders produced by a vapour phase reaction had considerable vacancies in both metal and nitrogen sublattices. The result shown in Fig. 5 may be interpreted as follows: the increase of a_0 by increase of the N/Nb ratio in the range of $N/Nb < 0.9$ may be due to the decrease of the vacancy at the nitrogen sublattice. The decrease of a_0 above $N/Nb = 0.9$ may be due to the increase of the vacancy at the niobium sublattice in addition to the vacancy at the nitrogen sublattice. The small a_0 in comparison with that of [7] near stoichiometric composition suggests strongly the presence of a large number of vacancies in both niobium and nitrogen sublattices. In order to examine the existence and thermal stability of vacancies, the powders A in Fig. 5 were heated in hydrogen atmosphere at 850° C for 30 min.* Using this heat treatment, the lattice constant and N/Nb ratio of the δ-NbN powders changed from A to B in Fig. 5. The increase of lattice constant indicates the existence of lattice vacancies in the as-produced powder A and their decreases by the annealing. The fact that point B is located between Curves 1 and 2 indicates that the NbN powders produced by a chemical vapour reaction have more vacancies than those produced by the nitridation of niobium metal.† As will be seen later, the superconducting transition temperature was raised by the annealing.

From the results mentioned above, the following reaction conditions give δ-NbN powders having the least vacancies in the present work: $T_M = 650$ to 800° C, $T_R = 1200$ to 1300° C and $[NH_3]/[NbCl_4] = 1.5$ to 4.

3.2. Electron microscopic observation

Fig. 6 shows the electron micrographs of δ-NbN powders. The particles are spherical and smaller than 50 nm. The particles produced at 1100° C are hollow. The particle size did not vary with $NbCl_4$ concentration (0.8 to 2.3%).

---

*It was recognized that the decomposition of NbN powder in hydrogen atmosphere began at 600° C and occurred vigorously at 1000° C.

†The concentration of vacancies in the NbN structure can be calculated from the density of NbN powder, the ratio N/Nb and the lattice constant. But it was difficult to measure the true density of the NbN powder produced in this system due to the presence of hollow particles.

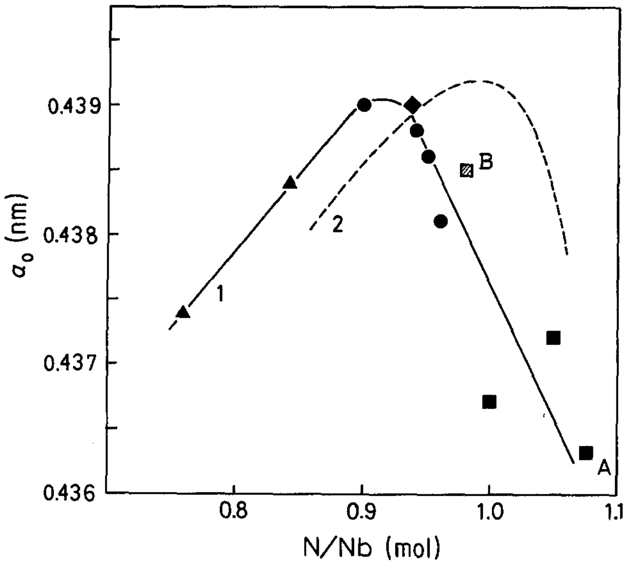

Figure 5 Lattice constant against N/Nb ratio. T_R: ■, 1100° C; ●, 1200° C; ◆, 1250° C; ▲, 1400° C. 1 —— this work; 2 ------ [8]; B ▨ annealed sample.

3.3 The particle formation process

The formation process of the nitride particles by vapour phase reaction of the MCl_x–NH_3–H_2 system (M: metal) can be classified into the following three types [11, 12]:

(i) Formation of adduct particles of reactants and their thermal decomposition into nitride.

(ii) Formation of nuclei of nitride and their growth into particles.

(iii) Formation of metal particles and their nitridation.

The particle formation process changes with the reaction conditions even in the same system and influences the properties of the resulting powders. Which formation process occurs is determined by the thermal stability of adduct particles of reactants and the ease of reducing metal chlorides.

The formation process of TiN powders by the vapour phase reaction of the $TiCl_4$–NH_3–N_2–H_2 system, which is very similar to the reaction system in the present study, changed with the mixing temperature (T_M) of $TiCl_4$ and NH_3. The formation of TiN powder takes place by Process (i) at $T_M < 250°$ C and by Process (ii) at $T_M > 600°$ C [11–13]. Fowles *et al.* [14] reported that the adduct between $NbCl_5$ and NH_3 decomposed to niobium nitride at 800° C. The present authors examined again the thermal decomposition of the adduct between $NbCl_5$ and NH_3 in Ar(47%)–H_2(47%)–NH_3(6%) atmosphere and found that the adduct (white) began to decompose at 300° C and changed colour as follows:

$$\text{orange } (450°\,C) \rightarrow \text{greenish black } (600°\,C) \rightarrow \rightarrow \text{black } (800°\,C).$$

The decomposition product was δ-NbN at 800° C. Otherwise, the dependences of the phase produced and the lattice constant of δ-NbN on the mixing temperature (T_M) were different between below and above 800° C (Fig. 2). This indicates the change of the formation process of NbN particle with the mixing temperature.

These results suggest that the formation of NbN particle takes place by Process (i) when the mixing temperature of $NbCl_4$ and NH_3 is below 800° C. That is, the process consists of the initial formation of $NbCl_4$–NH_3 adduct particles in the low temperature zone of reactor and their subsequent thermal decomposition into NbN particles in the high temperature zone as follows:

$$NbCl_4 + NH_3 \xrightarrow{<\sim 800°\,C} (NbCl_4 \cdot nNH_3)\text{ particle} \qquad (2)$$

$$(NbCl_4 \cdot nNH_3)\text{ particle} \xrightarrow{\geq \sim 800°\,C} NbN\text{ particle} \qquad (3)$$

The evolution of the decomposition gas in Step (3) might be responsible for the formation of the hollow particles as seen in the powder products at 1100° C (Fig. 6).

The ratio N/Nb of the powder produced by Process (i) may be determined by the ratio N/Nb of the adduct and the degree of its thermal decomposition. The increase of the ratio $[NH_3]/[NbCl_4]$ may increase the ratio N/Nb of the adduct

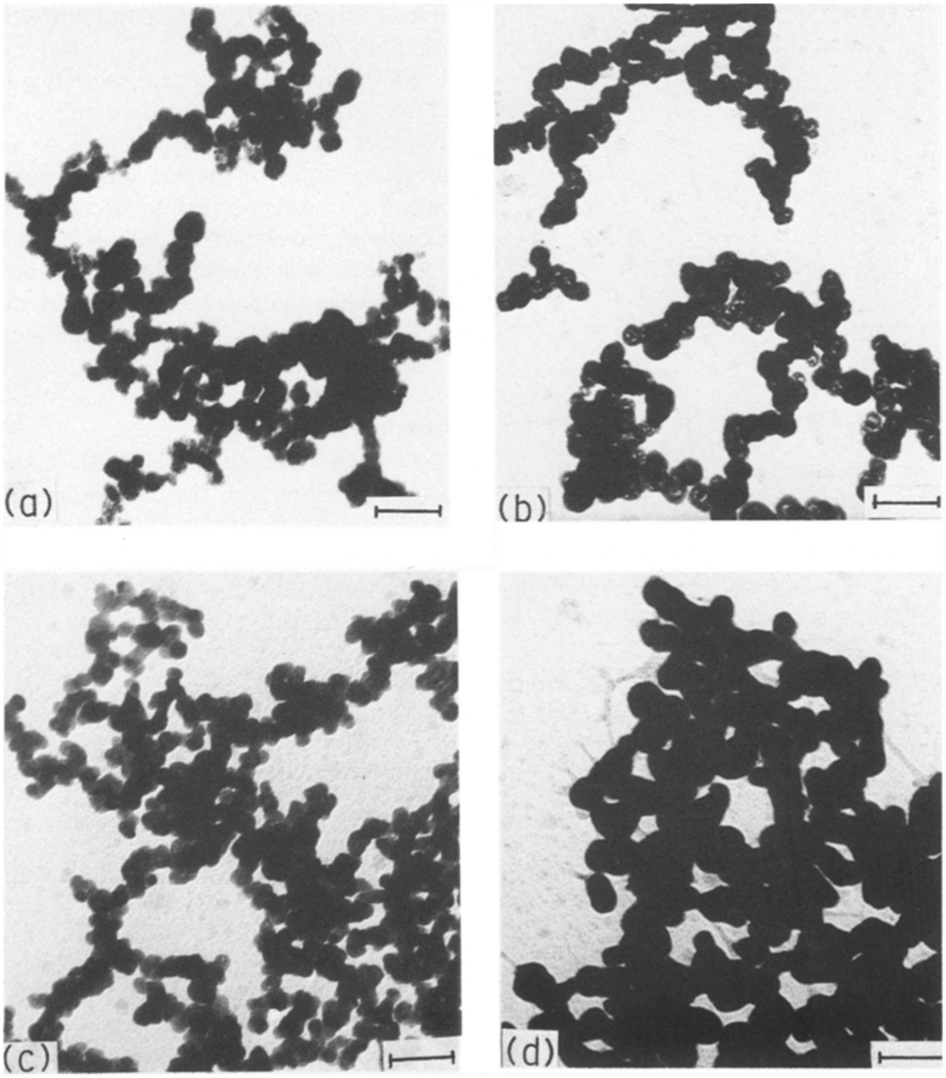

Figure 6 Electron micrographs of δ-NbN powders (marker = 0.1 μm). T_M = 800° C; T_R (a) 800° C; (b) 1100° C; (c) 1200° C; (d) 1400° C. For other conditions, see Fig. 3.

and thus the ratio N/Nb of the powder products as seen in Fig. 4. The increase of the reaction temperature may increase the degree of thermal decomposition of the NbN powder and result in the decrease of the ratio N/Nb. This was observed at $T_R > 1000$° C (Fig. 3). The reason why the ratio N/Nb was low at $T_R = 800$ and 900° C is under investigation.

On the other hand, when the mixing temperature is above 800° C, either Process (ii) or (iii) may become dominant for the particle formation. Of the two processes, Process (ii) is considered to be predominant at $T_M > 900$° C, because the degree of reduction of $NbCl_5$ by hydrogen was only 50% even at 1400° C [1] and metallic niobium was not produced even at $[NH_3]/[NbCl_4] = 1.2$ in the present work. The formation of the nitrogen-poor β-Nb_2N phase at high T_M as shown in Fig. 2 indicates the increased deposition rate of niobium in comparison with that of nitrogen. This may be due to the increased reactivity of $NbCl_4$ and the partial decomposition of NH_3 before mixing.

3.4. Superconducting transition temperature

Fig. 7 shows the variation of the resistance of NbN powder compacts with temperature. The resistance is expressed by normalized values for its normal

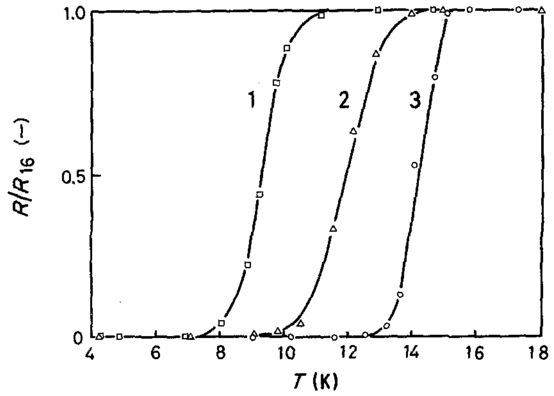

Figure 7 Variation of resistance of NbN powder compacts with temperature. 1, N/Nb = 0.78, $a_0 = 0.4375$ nm; 2, N/Nb = 0.87, $a_0 = 0.4385$ nm; 3, N/Nb = 0.90, $a_0 = 0.4390$ nm.

state ($T = 16$ K). The temperature at $R/R_{16} = 0.5$ was taken as T_c and the temperature range between $R/R_{16} = 0.75$ and $R/R_{16} = 0.25$ was taken as the transition width, ΔT_c.

Figure 8 shows the relation between T_c and the ratio N/Nb of δ-NbN. The vertical lines in the figure represent ΔT_c. The powder had the maximum T_c of 14.1 K at the N/Nb ratio = 0.9. NbN produced in the present work had a lower T_c than that reported by G. Horn *et al.* (dashed line). The difference in T_c between the two measurements increased with increase of the ratio N/Nb. This may be due to the high concentration of lattice vacancies at both niobium and nitrogen sublattices at N/Nb > 0.92 in the powder produced in this work. The release of vacancies by the annealing process increased T_c of the powder from 6 K (A in Fig. 8) to 13 K (B).

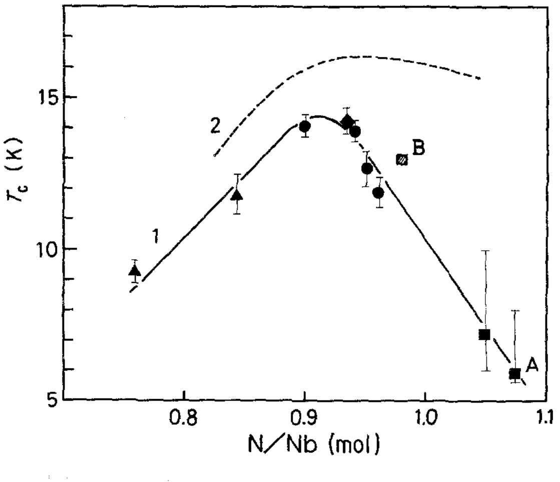

Figure 8 T_c against N/Nb ratio. Keys are the same as in Fig. 5. 1 —— this work; 2 ------ [9]; B ▨ annealed sample.

NbN film prepared by r.f. sputtering had T_c of 17.3 K [4], and T_c of vacancy-free stoichiometric δ-NbN is expexted to be 18 K [15]. As mentioned above, in order to prepare δ-NbN powder with high T_c, it is important to decrease the lattice vacancy and to control the ratio N/Nb in the range 0.9 to 1.0. Such niobium nitride may be obtained by annealing the powder produced by the vapour phase reaction or by adding a third element, such as carbon, to the reaction system.

Acknowledgements

The authors wish to thank Dr M. Takeo for his help and advice with the T_c measurements. This research was supported by the Scientific Research Aid of Ministry of Education (Grant 57116006). T_c was measured at the Applied Superconductivity Laboratory, Kyushu University.

References

1. A. KATO, T. WATARI and T. NAKAMATSU, *J. Less-Common Met.* **83** (1982) 227.
2. T. WATARI, T. NAKAMATSU and A. KATO, *ibid.* **91** (1983) L9.
3. M. MURAKAMI, T. WATARI and A. KATO, *ibid.* **92** (1983) L9.
4. K. S. KESKAR, T. YAMASHITA and Y. ONODERA, *Jpn. J. Appl. Phys.* **10** (1971) 370.
5. G. OYA and T. ONODERA, *J. Appl. Phys.* **45** (1974) 1389.
6. P. M. POWELL, W. J. SKOCPOL and M. TINKHAM, *ibid.* **48** (1977) 788.
7. R. W. GUARD, J. W. SAVAGE and D. G. SWARTHOUT, *Trans. Met. Soc. AIME* **239** (1967) 643.
8. G. BRAUER and H. KIRNER, *Z. Anorg. Allg. Chem.* **328** (1964) 34.
9. G. HORN and E. SAUR, *Z. Phys.* **210** (1968) 70.
10. J. HOJO, O. IWAMOTO, Y. MARUYAMA and A. KATO, *J. Less-Common Met.* **53** (1977) 265.
11. A. KATO, J. HOJO and Y. OKABE, *Mem. Faculty Eng. Kyushu Univ.* **41** (1981) 319.
12. A. KATO, J. HOJO and T. WATARI, 19th University Conference on Ceramics, North Carolina State University, November 1982, in press.
13. A. KATO, S. IWATA, J. HOJO and M. NAGANO, *Yogyo-Kyokai-Shi* **83** (1975) 453.
14. G. W. FOWLES and F. H. POLLARD, *J. Chem. Soc.* (1952) 4938.
15. T. H. GEBALLE, B. T. MATTHIAS, J. P. REMEIKA, A. M. CLOGSTON, V. B. COMPTON, J. P. MAITA and H. J. WILLIAMS, *Physics* **2** (1967) 293.

*Received 21 October
and accepted 3 November 1983*