

Preparation and Superconducting Properties of Niobium Carbonitride Wires

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Superconducting niobium carbonitride wires $\text{Nb}(\text{C}_y\text{N}_x)$ has been prepared by a diffusion process in two steps, first diffusing carbon from methane into niobium wires and then nitrogen into these carbonized samples. The optimum conditions for these preparations have been investigated in detail. All samples have been analysed quantitatively for C, N and Nb. The carbonizing as well as the following nitriding of the wires has been investigated under various conditions. The maximum of the transition temperature of the $\text{Nb}(\text{C}_y\text{N}_x)$ wires prepared by this two steps diffusion process is reached for the same composition y, x as for sintered samples. But the value is about 0.4 K lower.

1. Introduction

Niobium carbonitrides show high transition temperatures. Because of the complete miscibility of NbC and NbN the dependence of the critical temperature on the number of valence electrons pro atom, the lattice parameter and other crystal physical properties can be studied in this system over the whole range of compositions.

Matthias¹, Shulishova², Williams et al.³ and Pessall et al.⁴ investigated the NbC–NbN solid solutions systematically. They all prepared their samples by cold pressing NbN and NbC or Nb and NbC powders and subsequently sintering them in a furnace under N_2 atmosphere. The samples prepared in this way show a large porosity. Pessall reports of pores up to 30 vol%. Because of their large cross-section the sintered samples are not suitable for measurements of critical current densities in magnetic fields.

In the present investigation a method shall be described for the preparation of niobium carbonitrides by diffusion of carbon and nitrogen into compact niobium wires of 0.5 mm diameter which can be used for measurements of their critical data in magnetic fields.

2. Experimental Procedure

Niobium wires of 0.5 mm in diameter and 12 cm length are clamped inside water-cooled steel bombs and heated to 1600 °C by direct current in a methane atmosphere. The methane gas enters through a capillary tube on one side of the bomb and reacts with the hot niobium wire. Carbon dif-

fuses into the niobium and NbC is formed. The gaseous reaction products and the excessive methane are exhausted by a vacuum pump on the opposite side of the steel bomb. The pressure of the methane gas is indicated by a mercury pressure gauge.

Temperature measurements are carried out pyrometrically through a glass window in the steel bomb. The diffusing carbon increases the resistance of the Nb wire. In order to prevent a decrease of the sample temperature the heating voltage is controlled by means of a photodiode and an amplifier similar to that of Kauer and Hörster⁵. The desired temperature can be adjusted by a movable shield in front of the photodiode. The deviations of the adjusted temperatures were less than 30 °C during the reaction time in the methane atmosphere. When the diffusion of carbon has to be finished the supply of methane is interrupted and the steel bomb with the heated sample is evacuated for a short time down to 10^{-2} Torr. Finally the bomb is slowly filled with nitrogen up to a pressure of 101 atm. By the following heating at 1800 °C nitrogen diffuses into the wire. 22 hours later the current is switched off. The sample cools down to room temperature in about 1 minute.

3. Measurements

3.1. Chemical Analysis

All samples were analysed chemically to find out the exact composition. The ratio of nitrogen (x) is determined by a method described by Brauer and Kern⁶. The powdered sample is mixed with CuO and heated in a quartz tube up to 1000 °C in a flow of CO_2 . During this procedure Nb oxidizes



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and nitrogen is transported in the CO_2 flow into a gas-burette and collected under KOH.

To determine the carbon ratio (y), the powdered sample is oxidized in an oxygen flow at a temperature of 1400°C . The generated CO_2 is led into a solution of BaCl_2 . By means of a calomel electrode and a glass electrode the p_{H} of the solution is measured. The p_{H} value changes while BaCO_3 is precipitated. The original p_{H} is readjusted by electrolysis. In order to determine the amount of CO_2 the charge $\int I dt$ of the electrolyzing current is measured. This method is reported by Oelsen, Graue and Haase⁷.

The amount of niobium is determined by the increase of mass after heating $\text{Nb}(\text{C}, \text{N})$ in the atmosphere to about 1000°C . Niobium oxidizes to stoichiometric Nb_2O_5 .

3.2. Measurement of Critical Temperatures

The transition temperatures to superconductivity are measured by the resistivity of the samples in liquid hydrogen.

4. Results

4.1. Carbonizing Curves

Figure 1 shows data for three different carbonizing conditions. At first carbon is only contained in a surface layer. During a sufficient diffusion time in methane, however, the carbon layer extends all over the cross-section of the wire. The NbC layer splinters partly when the sample is cooled down to room temperature.

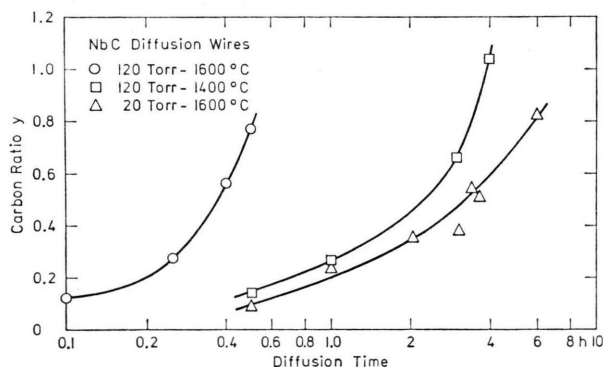


Fig. 1. Diffusion of carbon into niobium wires under various conditions.

X-ray patterns of the layer show the crystal structure of NbC and a lattice parameter $a = 4.4460 \text{ \AA}$. At 1600°C and 120 Torr CH_4 pressure

complete carbonizing takes place in 0.6 hours and the NbC sample is coated in a layer of carbon. The diffusion of carbon is delayed at a temperature of 1400°C .

No black carbon layer appears if the methane pressure is 20 Torr and diffusion takes place at 1600°C . After a reaction time of 10 hours the niobium wires are completely transformed into NbC. The NbC samples made in this way are dark greyly coloured.

4.2. Preparation and Investigation of NbN Wires

Diffused NbN wire samples of the highest critical temperatures⁸ are formed at diffusion temperatures

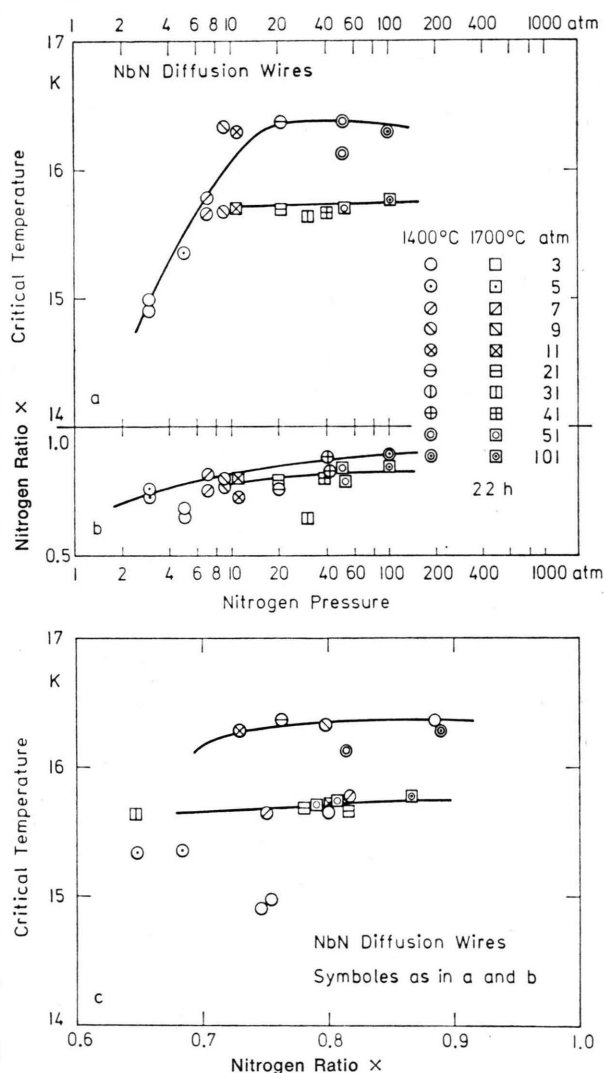


Fig. 2. Critical temperatures and nitrogen ratios x for NbN wires diffused under various conditions.

of 1400 °C with nitrogen pressures higher than 10 atm (Figure 2 a). NbN wires produced at less than 10 atm are not homogeneous. This is shown by their wide transition curves and their low critical temperatures. For the preparation of Nb(C,N) wires a diffusion temperature of 1400 °C in nitrogen has been found to be too low, so experiments were made at 1700 °C and 1800 °C. At 1800 °C the wires broke after some minutes of diffusion. The samples prepared at 1700 °C and various pressures show at equal nitrogen ratios lower critical temperatures than those prepared at 1400 °C (Figure 2 c).

At pressures between 10 and 100 atm NbN is formed in a composition NbN_{0.78} to NbN_{0.86}.

The dependence of the nitrogen ratio on the pressure at 1400 °C and 1700 °C is shown in Figure 2 b. At equal pressures the nitrogen ratios are somewhat higher at 1400 °C than at 1700 °C. With increasing pressure the nitrogen ratio increases.

4.3. Preparation and Investigation of Nb(C,N) Wires

Two series of Nb(C_yN_x) samples were prepared: The wires of the first series were heated at 120 Torr and 1600 °C in the methane flow for various periods of time, in order to adjust the desired amount of carbon. Subsequently the samples were diffused in nitrogen at 1800 °C and 31 atm. The critical temperatures of these samples are shown in Figure 3 a. The highest critical temperature is 17.2 K. Chemical analysis of carbon and nitrogen amounts are indicated in Table 1. All these samples show (x+y) values between 0.72 and 0.85. Be-

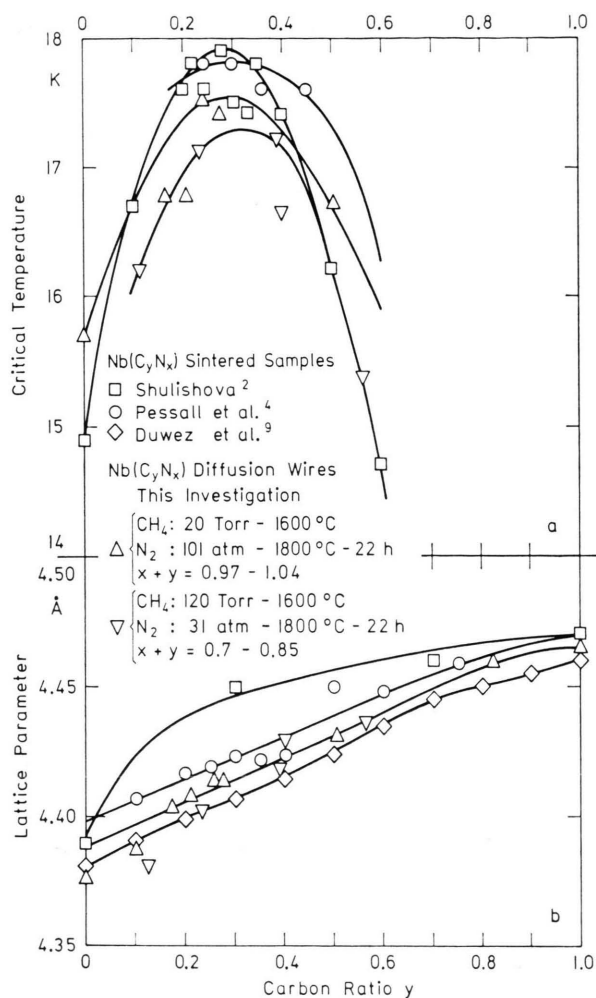


Fig. 3. Critical temperatures and lattice parameters of Nb(C_yN_x) sintered samples and Nb(C_yN_x) diffusion wires as a function of carbon ratio *y*.

Table 1. Diffusion conditions, compositions, critical temperatures and lattice parameters of Nb(C,N) wires.

Sample no.	Diffusion in:			C		N			T_c K	Lattice param. Å
	CH ₄ Press. Torr.	1600 °C Time h	N ₂ 22 h Press. atm	mol %	<i>y</i>	mol %	<i>x</i>	<i>x</i> + <i>y</i>		
230	120	0.75	31	23.46	0.40	17.69	0.30	0.70	16.64	4.430
231	120	0.55	31	22.33	0.39	20.31	0.35	0.74	17.21	4.418
232	120	0.30	31	32.54	0.56	9.66	0.17	0.73	15.36	4.436
234	120	0.20	31	13.18	0.24	27.72	0.47	0.71	17.13	4.402
238	120	0.10	31	6.63	0.12	39.33	0.73	0.85	16.18	4.381
294	20	1.95	101	14.29	0.27	35.16	0.72	0.99	17.42	4.414
296	20	0.50	101	8.08	0.17	43.15	0.88	1.04	16.77	4.403
297	20	4.00	101	41.86	0.82	7.09	0.14	0.96	<14.00	4.460
278	20	1.25	101	10.43	0.21	39.54	0.79	1.00	16.76	4.408
279	20	3.54	101	25.52	0.50	23.83	0.47	0.98	16.71	4.431
281	20	0.80	101	11.86	0.25	37.67	0.75	1.00	17.53	4.414
283	20	0.25	101	5.06	0.10	44.34	0.88	0.98	16.51	4.388

cause of the large deviation from stoichiometry a second series of $\text{Nb}(\text{C}_y\text{N}_x)$ wires was made with the following diffusion conditions:

CH_4 : 20 Torr 1600 °C;
 N_2 : 101 atm 1800 °C, 22 h.

The samples prepared this way showed higher critical temperatures. The highest one measured was 17.53 K. The composition of this sample was $\text{NbC}_{0.25}\text{N}_{0.75}$. All wires of this series were nearly stoichiometric ($0.97 < x + y < 1.04$).

The lattice parameters (Fig. 3 b) of the first series are between 4.380 Å and 4.440 Å. Those of the second are larger in agreement with Pessall et al.⁴ and Duwez and Odell⁹.

In the phase diagram¹⁰ all $\text{Nb}(\text{C}, \text{N})$ samples are registered (Figure 4). The samples of the first series are partly two phase, but all samples of the second series are single phase. Micrographs of those wires show two till five crystal grains on the cross-section and no layer structure.

5. Discussion

5.1. Niobium Nitride

T_c of NbN depends on the diffusion temperature. NbN_x samples with the same nitrogen ratio can be prepared at different temperatures. The critical temperature of wires made at 1700 °C with x values between 0.8 and 0.9 is 0.5 K lower than that of

wires diffused at 1400 °C with the same x value. The critical temperature of both series of NbN wires increases by 0.1 K if the x value is changed from 0.7 to 0.9.

5.2. Niobium Carbonitride

T_c of $\text{Nb}(\text{C}_y\text{N}_x)$ wires probably does not only depend on the chemical composition but also on the diffusion temperature. The homogenisation of the sample over the cross-section needs high preparation temperatures. On the other hand the decomposition pressure of NbN increases with temperature. Therefore high N_2 pressures are necessary to get stoichiometric samples. All diffusion wires plotted in Fig. 3 a were prepared at 1800 °C. Pessall sintered his samples at 1525 °C and Shulishova at 1200 °C to 1400 °C. In order to study the influence of the diffusion temperature on T_c , some samples were tempered at 1400 °C for 2 hours under N_2 pressure after the homogenizing process, but no increase of T_c was observed.

The maximum of T_c is found at the same chemical composition as reported by Pessall and Shulishova, but T_c is 0.4 K lower. Shulishova observes the highest T_c values (17.9 K) only for samples with stoichiometric composition. But Pessall reaches $T_c = 17.8$ K with a sample of $x + y = 0.9$. All wires of the first series of this investigation are nearly stoichiometric ($0.97 < x + y < 1.04$). The series with $x + y \approx 0.75$ shows lower T_c values as re-

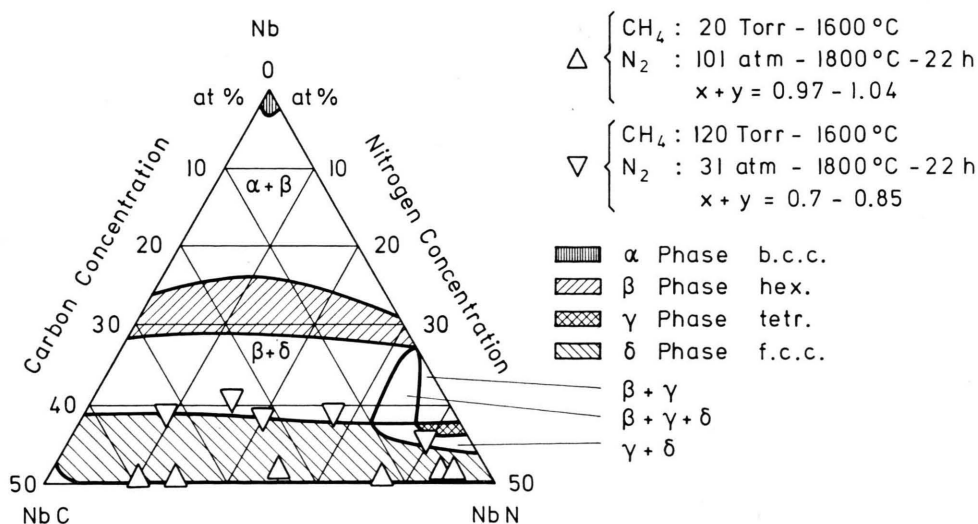


Fig. 4. Phase diagram of the Nb—NbC—NbN pseudo-ternary system.

ported by Shulishova. As the transition temperatures of the NbN wires with $T_c = 16.37$ K indicate, the purity of the starting materials Nb and N_2 is sufficient. The methane gas was of 99.95% purity.

A tempering process in the temperature region of 1200°C to 1600°C under N_2 pressure, following the process of homogenisation at 1800°C , will

probably increase T_c to 17.9 K as reported by Shulishova and Pessall.

Acknowledgements

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