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SUPERCONDUCTIVITY OF CUBIC NIOBIUM CARBO-NITRIDES

M.W. Williams, K.M. Ralls, and M. R. Pickus

September 1966
SUPERCONDUCTIVITY OF CUBIC NIOMIUM CARBO-NITRIDES

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ABSTRACT

An investigation has been made of the superconductive properties of the niobium-carbon-nitrogen ternary system. These compounds always have a range of composition, and previous investigators have often neglected the effect of stoichiometry. Both critical temperature \( T_c \) and upper critical field \( H_{c2} \) are dependent on composition, although not in the same way. The trend of \( H_{c2} \) at 4.2 K with decreasing nitrogen content is always down. The maximum \( T_c \) (17.8 K) occurs for nearly stoichiometric compounds having a C/Nb ratio of about 0.3. The critical temperature of substoichiometric NbN, which contains a small amount of carbon rather than the more common impurity oxygen, is 17.2-17.3 K.
INTRODUCTION

Cubic niobium carbo-nitrides have been of interest recently because of their high critical temperatures and magnetic fields. A maximum critical temperature of 17.8°K has been reported for a composition of 25 to 30 mol.% NbC in the NbC-NbN pseudo-binary system.\(^1,2,3,4\) A maximum critical field of 120 kG has been observed at somewhat lower NbC content.\(^2\)

The transition metal-interstitial compounds are somewhat difficult to study because variations from stoichiometric compositions often strongly affect the superconductive properties. For instance, NbC and TaC exhibit a sharp decrease in critical temperature with departure from stoichiometry.\(^5\) These compounds always have a range of homogeneity, which has led to ambiguous results in many previous studies.

In our investigation of the niobium-carbon-nitrogen ternary system, a primary objective was control of composition. A careful preparative technique and thorough investigations of the specimens by x-ray diffraction and chemical analyses have made possible a clearer description of superconductive properties in this ternary system.

The maximum \(T_c (17.8°K)\) was found for compositions near 30% NbC in NbN, in agreement with previous studies. \(H_c^2\) was found always to decrease with decreasing nitrogen content (either due to departure from stoichiometry or to substitution of carbon for nitrogen). The maximum critical field (132 kG) found in our investigation is the highest yet reported for this ternary system.
PREPARATION PROCEDURE

Powders of Nb* and NbC† were weighed to give nominal compositions of Nb, NbC₂, NbC₃, and NbC₅ and were dry mixed by tumbling. These powders were coated with polystyrene and extruded as 1/8 in. rods which were broken into 2 in. lengths. The firing procedure was designed to vaporize the styrene and to sinter the rods to a porous mixture of Nb and Nb₂C.⁶

The nitriding reaction was carried out at temperatures of 1280, 1360, or 1470°C, at pressures of 1, 10, 100, 760 or 7600 torr for either 4 or 8 hours. The nitriding procedure, described in more detail elsewhere,⁷ tended to minimize oxygen contamination but could have permitted a change in the carbon content during firing. To prevent nitrogen loss, vacuum sintering of the nitrided specimens was avoided.

COMPOSITIONS

The nitrogen content of the samples was determined from the weight gain of the specimens during nitriding. The carbon content was determined by the amount of NbC in the mixed powders before extrusion. The NbC had a lattice parameter of 4.4700±0.0005, corresponding to a composition slightly under stoichiometry.⁸ The initial carbon contents were therefore somewhat below the nominal starting compositions.

As a check on both the carbon and nitrogen contents, several samples were analyzed chemically. The results of the analyses of the sintered but not nitrided compositions (Table I) indicated that the nominally pure niobium had gained approximately 2 at.% carbon during the processing prior to the nitriding treatment, while the other three compositions had lower

---

* 99.9%, -325 mesh Nb powder from Kawecki Chemical Company, Boyertown, Pa.
† 99.9%, -325 mesh NbC powder from Pansteal Metallurgical Corp., North Chicago, Illinois.
carbon contents than their starting compositions. A metallographic study of the sintered niobium revealed a small amount (~6 vol.%) of uniformly distributed, discontinuous second phase, most likely Nb2C.

A set of four nitrided samples of different carbon compositions was analyzed for carbon, nitrogen, and oxygen (Table II). The carbon and oxygen contents were nearly the same as the amounts in the sintered but not nitrided samples. The nitrogen contents, however, were not in agreement with weight gain data. As a further check, two pairs of identical samples were analyzed (Table III). In these samples the carbon and oxygen analyses were consistent, while the nitrogen analyses disagreed by as much as 20%.

Because of the disparity in the results of the nitrogen analyses, the weight gain was taken as representative of the bulk composition. The carbon contents of Table I were assumed to be correct and not changed during the nitriding reaction.

Two nitrides prepared at 10 atm were also analyzed and were found to be somewhat contaminated by oxygen (on the order of 0.2 to 0.3 wt.%, i.e., about 1 at.%). A higher oxygen content was to be expected in samples prepared at higher pressures since there was more oxygen available in the atmosphere surrounding the samples. This higher oxygen content was taken into account in the consideration of the physical properties of these samples.

As expected, the nitrogen content increased with nitriding pressure, but was not appreciably affected by the nitriding time. This fact implies that at least a gas-solid equilibrium was obtained, although there is the possibility that complete homogeneity was not reached in the solid.

In almost all cases, the greatest amount of nitrogen was gained at 1280°C (Fig. 1) and the smallest amount at 1470°C. Although there are not
constant pressure, the trend does indicate that the departure of the nitrogen content from ideal stoichiometry becomes significant at the temperatures studied in this investigation.

X-RAY RESULTS

Powder patterns of all samples were taken on a Picker diffractometer with nickel filtered copper radiation ($\lambda_{CuK\alpha_1} = 1.54051\AA$). The predominantly cubic niobium nitrides were also checked by the Debye-Scherrer technique for a more precise lattice parameter determination.

The specimens prepared at either 760 or 7600 torr were almost always cubic. In only two of the samples (nitrides prepared at 760 torr and 1470°C) was there any indication of a second phase. This second phase was also cubic but with a lattice parameter of 4.45, indicating it might be $\text{Nb}(C,N)$. At 100 torr the samples with intermediate carbon content ($C/Nb = 0.2$ or $0.3$) contained significant amounts of two cubic phases with lattice parameters near 4.39 and 4.42Å. The specimen with the highest carbon content ($C/Nb = 0.5$) contained only one cubic phase. At 10 torr, the tetragonal nitride $\text{Nb}_4\text{N}_3$ was a significant phase. At 1 torr the hexagonal phase $\text{Nb}_2(C,N)$ predominated.

CRITICAL TEMPERATURES

Critical temperatures were measured by the technique of Merriam and Von Herzen. Many transitions, particularly those above 17°K, took place over 0.1 or 0.2°K. In some transitions, there was a "low-temperature tail" characteristic of these compounds, but in general the transitions were quite sharp.

Our results for the samples prepared at 760 torr (Fig. 2b) are generally in agreement with those of Pessall et al., except for the
critical temperature of NbN. Our results indicate a higher critical
temperature for NbN than previously reported.

The dependence of $T_c$ on C/Nb ratio is similar for samples prepared
at the three highest nitriding pressures. The broad maximum in critical
temperature near 30% NbC has been confirmed for three different nitriding
pressures. Whereas slightly different $T_c$ values resulted for the
different nitriding temperatures, the spread of $T_c$ midpoints for specimens
with constant C/Nb was usually less than 0.4°K for 760 torr and for
7600 torr in spite of the apparent differences in nitrogen content (Fig.
1a,b,c,d). For 100 torr the specimens nitried at 1360°C had the highest
critical temperatures and those nitried at 1470°C had the lowest critical
temperatures, although the spread in midpoints was usually less than
0.6°K for specimens with constant C/Nb. Therefore, for clarity in the
figures, the critical temperature data presented (Figs. 2a,b,c and
3a,b,c,d) are averaged over the three nitriding temperatures. It should
be pointed out that the total interstitial contents of samples of all
four carbon compositions were approximately the same for samples prepared
at constant pressures of 100, 760, or 7600 torr (Fig. 1a,b,c,d). Figures
2a,b,c therefore approximate constant stoichiometry plots.

All critical temperatures of the cubic samples near stoichiometry
were near 17 to 17.8°K. All three of the nominally pure nitrides pre-
pared at 7600 torr had lower values of $T_c$ than those prepared at 760
torr (Fig. 3a). These lower transitions could have been due in part to
the oxygen contamination of the 7600 torr specimens.

The effect of pressure on the carbo-nitrides was less pronounced
(Fig. 3b,c,d). While the $T_c$ of the nitride prepared at 7600 torr was
lower than that of the nitride prepared at 760 torr, the critical tempera-
tures of the samples with C/Nb = 0.2 prepared at those two pressures were
essentially the same; the other two compositions showed a higher transition temperature in samples nitrided at the higher pressure.

CRITICAL MAGNETIC FIELDS

Critical fields \( H_{c2} \) at 4.2 K were measured by a pulsed field magnetization technique. \(^{11}\) As a check, a few transitions were measured by resistive methods. The results agreed within 2-3%.

The variation of \( H_{c2} \) with nitriding pressure was different from the trend of \( T_c \) in that the critical field always increased as the nitriding pressure increased (Fig. 3a,b,c,d). Even in the cases in which the transition temperature began to decrease with increasing pressure, the critical magnetic field continued to increase.

As a function of carbon content, \( H_{c2} \) showed a different trend than had been found by other investigators. At all pressures, except 10 torr, the pure nitride possessed the highest critical field. The trend in critical field was downward with increasing carbon content (Fig. 4a,b,c). The highest critical field found in this investigation was 132 kG for the nitride fired at 1280 °C at 7600 torr for 4 hrs.

It should perhaps be mentioned that the critical fields of our specimens nitrided at 760 torr generally agree quite well with the fields reported by Pessall et al.\(^2\) The exception is the critical magnetic field of the pure nitride. We believe that the critical field of NbN is 118-132 kG, and is therefore the highest in the ternary system. We therefore contend that there is no maximum critical field at an intermediate composition in the NbC-NbN pseudo-binary system.
DISCUSSION

There are two possible explanations for the existence of two phases in the low stoichiometry portion of the cubic solid solution range: an equilibrium miscibility gap or a non-equilibrium situation in the solid. Since the starting material for the intermediate carbon contents was a mixture of Nb and Nb$_2$C, the final result after nitriding could be a mixture of phases with compositions near NbN and NbC$_{0.5}$N$_{0.5}$. If there had not been enough time for diffusion to occur, these phases would remain unmixed.

An isothermal diagram (Fig. 5) indicates that only the samples prepared at low nitrogen pressures are in nonequilibrium states. It is not possible to draw an equilibrium phase diagram with the points as shown in Fig. 5. The three phase field, which must exist between the two cubic phase region and the cubic plus tetragonal region did not appear in any of our samples and cannot be drawn on the diagram in conformance with the thermodynamic requirements of such a field. Because the x-ray patterns did indicate a single phase in the samples prepared at higher pressures, we believe that these samples are near equilibrium.

In the presentation of our data, the bulk composition of the samples based on weight gain has been used. This composition is somewhat ambiguous in samples containing more than one phase, but we do consider it a representation accurate enough to indicate trends in the data. A better parameter than composition might be the lattice parameter. In the event of inhomogeneity in the specimen, the x-ray data would reflect the most abundant phase while the superconducting transitions would tend to show all compositions, weighting the size of the transition signal according to the volume of the phases. Indeed, two transitions did appear in some
samples containing two phases. Since the lattice parameter can be varied
either by stoichiometry or by carbon content, there is no accurate way to
determine the composition of a cubic phase coexisting with another phase
solely on the basis of lattice parameter. Furthermore, since the samples
prepared at or above 100 torr are largely single phase, we consider the
weight gain to be a reasonably accurate parameter on which to base our
discussion.

One of the important parameters considered in connection with super-
conductivity is the ratio of electrons per atom. One critical value is
generally taken to be about 4.75. Since these non-stoichiometric compounds
have many vacant interstitial sites which do not contribute electrons, the
ratio used for these samples was electrons per niobium atom. This ratio
changes with stoichiometry and is equal to twice the value of electrons
per atomic site based on two atomic sites per formula \( \text{NbC}_x \text{N}_y \). The choice
of this parameter is based on the hypothesis that the fcc niobium d-band
is of primary importance in determining the superconducting properties
of the niobium carbo-nitrides. It should be noted, however, that
Geballe et al. have recently proposed that these materials are sp-band
superconductors with strong electron-phonon coupling. 13

Figures 6a,b,c,d, show critical temperature as a function of elec-
trons per atom based on the bulk composition. The NbN shows a broad
maximum in \( T_c \) at 9.5-9.9 valence electrons per niobium atom. The decrease
of \( T_c \) (Fig. 6a) for higher values of \( O/Nb \) is probably due to the higher
oxygen contents for the NbN specimens prepared at 7600 torr. Nevertheless,
when data existing in the literature are considered in addition to these

* cf. ref. 7. Compositions determined from lattice parameter data for
NbN give the maximum \( T_c \) at about NbN \( 0.93\) - NbN \( 0.96 \), 9.65-9.8 valence
electrons per niobium atom.
data presented here, it appears that the decrease of $T_c$ is real. The carbon-containing specimens also show broad maxima in $T_c$ with valence electrons per niobium atom (Figs. 6b,c,d); however, there is almost no indication of decreasing $T_c$ at higher values of C/Nb. This may be due to the limited range of composition attained here since few carbo-nitride samples approached ideal stoichiometry. Although there is considerable overlap of $e/Nb$ for the $T_c$ maxima, they are so broad and indefinite that it is impossible to say they occur at the same $e/Nb$ value. Furthermore, reduction of the data in Fig. 6a,b,c,d to a single master curve is not possible. This is reasonable in view of the clearly established importance of the effect of lattice dilatation.

Whereas $e/Nb$ does not uniquely determine $T_c$, it does appear that increasing $e/Nb$ through nitriding at pressures higher than 7600 torr will raise $T_c$ further for three of the carbon contents reported here (Fig. 3b,c,d). It may be noted that the dependence of $T_c$ on both pressure and carbon content is somewhat different from the behavior of $H_{c2}$. Once the crystal structure is predominantly cubic ($\log P$ (torr) > 2) the variation in $T_c$ is proportionately less than that of $H_{c2}$. $H_{c2}$ decreases quite rapidly either with decreasing N/Nb and constant carbon content or with increasing C/Nb for constant nitriding pressure. Furthermore, the optimum composition for high critical fields is near the stoichiometric nitride rather than the carbo-nitrides which have the highest critical temperature.

$H_{c2}$ can be described in terms of the product of electronic specific heat coefficient ($\gamma$), critical temperature, and normal resistivity ($\rho_n$). $T_c$ increases slightly with increasing carbon content at constant nitriding pressure. This fact implies that the product $\rho_n \gamma$ must be decreasing as
carbon content increases. Because of the unfavorable sample shape (1/8" dia. by 1" length) and unknown effective cross sections no resistivity measurements were made. Nevertheless the high $H_{c2}$ for NbN prepared at 7600 torr (Fig. 4c) is probably related to a high value of $\rho_n$ due to the oxygen content.

There are indications based largely on empirical correlations that the density of states (and consequently, $\gamma$) decreases between the compositions NbN and NbC. Extensive measurements of the electronic specific heat in this ternary system have not been made. Therefore, any attempt to describe the variation in critical field with composition in terms of $\gamma$ and $\rho_n$ would be highly speculative. Recent experimental determinations of $\gamma$ for a few niobium nitrides, niobium carbides and a niobium carbo-nitride gave surprisingly low values which did not vary in the same sense as $T_c/\Theta_D$. If cubic niobium carbo-nitrides are strong coupling superconductors, then the dependence of $H_{c2}$ upon $\gamma$, $\rho_n$ and $T_c$ cannot be specified.

**CONCLUSIONS**

Critical temperatures and upper critical fields for cubic niobium carbo-nitrides both depend upon composition whether it is varied by substitution of carbon for nitrogen or by deviation from stoichiometry. The variation of $H_{c2}$ with composition is not identical to that of $T_c$. The maximum critical temperature (17.8°K) occurs for nearly stoichiometric carbo-nitrides with C/Nb ≥ 0.3, although niobium nitride (containing C/Nb = 0.026 and O/Nb = 0.002) prepared at 760 torr has a critical temperature nearly as high (17.2-17.3°K). The maximum critical fields at 4.2°K (118-152 kG) occur for niobium nitride prepared at 760-7000 torr. Whereas the higher value of $H_{c2}$ may be attributed to slight oxygen
contamination, the 118 KG value resulted for niobium nitride containing a very low oxygen content (O/Nb ≤ 0.001). We therefore believe that the optimum composition for a high \( H_c \) is the "pure" niobium nitride and that any departure from this composition will result in a lowering of the critical field.

ACKNOWLEDGMENTS

The authors would like to express their appreciation to Prof. Earl R. Parker and Prof. Victor F. Zackay for their interest in this investigation, and to Mr. Masaki Suenaga for his assistance in the critical field measurements.

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REFERENCES


Table I  Analyzed Compositions Before Nitriding

<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Nb</th>
<th>NbC.2</th>
<th>NbC.3</th>
<th>NbC.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (wt.%)</td>
<td>.54</td>
<td>2.3</td>
<td>3.5</td>
<td>5.7</td>
</tr>
<tr>
<td>O (wt.%)</td>
<td>&lt;.001</td>
<td>.018</td>
<td>.020</td>
<td>.015</td>
</tr>
<tr>
<td>(C/Nb)</td>
<td>.026</td>
<td>.183</td>
<td>.280</td>
<td>.466</td>
</tr>
</tbody>
</table>

Performed by Anamet Laboratories, Berkeley, California. Carbon determined by combustion; oxygen determined by vacuum fusion.

Table II  Analyzed Compositions After Nitriding 1360°C, 4 hrs, 760 torr

<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>NbN</th>
<th>NbN.C.2</th>
<th>NbN.C.3</th>
<th>NbN.C.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (wt.%)</td>
<td>.266</td>
<td>2.26</td>
<td>3.26</td>
<td>5.76</td>
</tr>
<tr>
<td>N (wt.%)</td>
<td>12.76</td>
<td>9.67</td>
<td>7.76</td>
<td>5.10</td>
</tr>
<tr>
<td>O (wt.%)</td>
<td>.031</td>
<td>&lt;.005</td>
<td>&lt;.005</td>
<td>&lt;.005</td>
</tr>
</tbody>
</table>

Formula based on analysis

\[
\text{NbN.} .969 \text{C.} .023 \quad \text{NbN.} .726 \text{C.} .200 \quad \text{NbN.} .576 \text{C.} .281 \quad \text{NbN.} .579 \text{C.} .511
\]

Formula based on carbon analysis and weight gain

\[
\text{NbN.} .919 \text{C.} .026 \quad \text{NbN.} .745 \text{C.} .183 \quad \text{NbN.} .697 \text{C.} .280 \quad \text{NbN.} .466 \text{C.} .566
\]

Performed by Oak Ridge National Laboratories; nitrogen and oxygen determined by vacuum fusion.
### Table III  Analyzed Compositions of Identical Samples*

<table>
<thead>
<tr>
<th>Nitriding Conditions</th>
<th>Sample Number</th>
<th>C (wt.%)</th>
<th>N₂ (wt.%)</th>
<th>O₂ (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1280°C, 100 torr</td>
<td>1</td>
<td>0.28%±.015</td>
<td>11.4%±.5</td>
<td>0.03%±.005</td>
</tr>
<tr>
<td>8 hrs.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1280°C, 100 torr</td>
<td>2</td>
<td>0.30%</td>
<td>12.4%</td>
<td>0.02%</td>
</tr>
<tr>
<td>8 hrs.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1280°C, 10 torr</td>
<td>3</td>
<td>0.59%</td>
<td>12.6%</td>
<td>0.05%</td>
</tr>
<tr>
<td>4 hrs.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1280°C, 10 torr</td>
<td>4</td>
<td>0.58%</td>
<td>10.5%</td>
<td>0.08%</td>
</tr>
<tr>
<td>4 hrs.</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

*Performed by Ananet Laboratories, Berkeley, California.
Carbon determined by combustion.
Oxygen and nitrogen determined by vacuum fusion.
FIGURE CAPTIONS

Fig. 1 The dependence of nitrogen to niobium atomic ratio on nitriding pressure for four different carbon contents. a) C/Nb = 0; b) C/Nb = 0.2; c) C/Nb = 0.5; d) C/Nb = 0.5.

Fig. 2 The variation of critical temperature ($T_c$) with carbon content at constant nitriding pressure. a) $P = 100$ torr; b) $P = 760$ torr; c) $P = 7600$ torr. ◮ Present investigation; □ Pessall et al.

Fig. 3 The variation of critical temperature ($T_c$) and critical magnetic field ($H_{c2}$) at 4.2°K with nitriding pressure. a) C/Nb = 0; b) C/Nb = 0.2; c) C/Nb = 0.5; d) C/Nb = 0.5.

Fig. 4 The variation of critical field ($H_{c2}$) at 4.2°K with carbon content at constant nitriding pressures. a) $P = 100$ torr; b) $P = 760$ torr; c) $P = 7600$ torr. ◮ Present investigation; □ Pessall et al.

Fig. 5 Isothermal section (1470°C) showing compositions and phases found in this investigation. ◮ cubic; △ tetragonal; ○ hexagonal; □ 2 cubic; △ tetragonal and cubic; ◰ hexagonal and cubic.

Fig. 6 The dependence of critical temperature ($T_c$) on electrons per niobium atom. a) C/Nb = 0; b) C/Nb = 0.2; c) C/Nb = 0.5; d) C/Nb = 0.5.
Fig. 1 (a, b)
Fig. 1 (c, d)
Fig. 2 (a,b,c)
Fig. 3 (b)
Fig. 3c
Fig. 3 (a)
Fig. 4 (a, b, c)
Fig. 5
Fig. 6 (a)
Fig. 6 (d) MUB-C49

\[
\frac{C}{Nb} = 0.5
\]
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