AD-751 545

DEVELOPMENT ON PROCESS FOR PRODUCING CONTINUOUS FINE DIAMETER FILAMENTS OF SUPERCONDUCTORS

James Economy, et al

Carborundum Company

Prepared for:

Air Force Materials Laboratory

September 1972

DISTRIBUTED BY:

National Technical Information Service U. S. DEPARTMENT OF COMMERCE 5285 Port Royal Road, Springfield Va. 22151 AD 75154

1

Á

Carlos Carlos Contest

のないたいない

DEVELOPMENT ON PROCESS FOR PRODUCING CONTINUOUS FINE DIAMETER FILAMENTS OF SUPERCONDUCTORS

James Economy, Ruey Yuan Lin, William D. Smith, C. K. Jun

The C. rborundum Company Niagara Falls, New York 14302

Technical Report AFML-TR-72-189



September 1972

Details of illustrations in this document may be better studied on microfiche

Approved for public release; distribution unlimited.

Reproduced by NATIONAL TECHNICAL INFORMATION SERVICE US Department of Commerce Springheld VA 22131

Air Force Materials Laboratory Air Force Systems Command Wright-Patterson Air Force Base, Ohio

NOTICE

1.4

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

20 3115 617 HTIS 003 1 5 CED#UDI - APU JUSTIFICATION 27 LISTEDUNON ARANDERT Dist, Kittig a. 1 a. em.

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

	N		
Unclassified	\$ 2 *		
Security Classification	NT CONTROL DATA	PLD	
(Security classification of title, body of abstract a	and indexing ennotation mus	- K & D t be entered when th	e overall report la clas
1. ORIGINATING ACTIVITY (Corporate author)		28. REPORT	SECURITY CLASSIFIC
The Carborundum Company Niagara Falls, New York 14302		26. GROUP	Juciassilled
			N/A
J. REPORT TITLE			
Development on Process For Product	ing Continuous Fi	ine Diameter	Filaments of
4. DESCRIPTIVE NOTES (Type of report and inclusive date	re) to Tulu 1 1072		
FIRAL REPORT JULY 1, 19/1 5. AUTHOR(S) (First name, middle initial, last name)	LU JULY 1, 19/2		
James Economy, Ruey Yuan Lin			
William D. Smith, C. K. Jun			
B. REPORT DATE	78. TOTAL N	IO. OF PAGES	7b. NO. OF REFS
August 1972	66	5	20
F33615-71-C-1709	98. ORIGINA	TOR'S REPORT NU	IMBER(\$)
6. PROJECT NO. 7371		AFML-TR-7	2–189
c. 03	D. OTHER	EPORT NO(S) (Any	othe' numbers that may
	this repor	1)	
<u>d. 24</u>		N/A	
N/A	12. SPONSOF AFML/I	ING MILITARY AC	TIVITY
	wrigh	c-Patterson	AFB, UNIO 454
A process to produce the cont both carbon and boron nitride prec converting chemically the precurso pentachloride in the presence of h yarns produced were characterized and their surface structures. Cri the superconductive filaments made the filaments were determined to b to prepare filaments with high fle	inuous niobium ca ursors was develor yarns into niob ydrogen and nitro by their supercost tical temperature by this method. 0 0.4-1.0 x 10 ⁵ exibility and str	arbonitride oped. The p bium carboni ogen. The s nducting and es up to 19 The critic amp/cm ² in z ength were a	filament yarn rocess involve trides with ni uperconductive mechanical pr K were observe al currents of ero field. Pr lso developed.

ومتنافيا فلوغ حادثتهم منابط المناقع معاراة فلالاممط معاسفه حناقه والمعرف معرفهم

,

KEY WORDS T	1 6101	(.	LIN	KB	1 1 1 1	xr I
	ROLE	WT	ROLE	WT	ROLE	WT
Filamentary Superconductors						
Niobium Nitride Superconductors						
Niobium Carbide Superconductors						
Low AC Loss Superconductors						
Carbon Fibers						
Boron Nitride Fibers						
High Field Superconductors						
High Transition Temperature Superconductors						
						Į
		1				[
						ļ
						I
	Un	class:	Lfied	[┉┉┉┉┉╢	أشبيه

DEVELOPMENT ON PROCESS FOR PRODUCING CONTINUOUS FINE DIAMETER FILAMENTS OF SUPERCONDUCTORS

82

AND SHEERINGS

× ., 70

· · · · 26

NC 5375

15 21 2227

「「ようなない」のである

V. 5. 72

James Economy, Ruey Yuan Lin, William D. Smith, C. K. Jun

Approved for public release; distribution unlimited.

FOREWORD

This is the final technical management report prepared by The Carborundum Company under Contract F33615-71-C-1709 for the Air Force Materials Laboratory (AFML). Dr. Melvin C. Ohmer was the Project Engineer. The report covers the period of July 1, 1971 through June 30, 1972.

The work was performed in the Research Branch of the Research and Development Division at Niagara Falls, New York. James Economy was the Program Manager and R. Y. Lin was the Project Leader. W. D. Smith and C. K. Jun were the Project Scientists. G. DeMunda actively made contributions to the experimental work.

The technical report has been reviewed and is approved.

CHARLES E. EHRENFRIED

Major, USAF Chief, Solid State Maperials Branch Electromagnetic Materials Division Air Force Materials Laboratory

ABSTRACT

のないないないで

A process to produce the continuous niobium carbonitride filat yarn from both carbon and boron nitride precursors was developed. The process involved converting chemically the precursor yarns into niobium carbonitrides with niobium pentachloride in the presence of hydrogen and nitrogen. The superconductive filament yarns produced were characterized by their superconducting and mechanical properties and their surface structures. Critical temperatures up to 19 K were observed for the superconductive filaments made by this method. The critical currents of some of the filaments were determined to be 0.4-1.0 x 10^5 amp/cm² in zero field. Procedures to prepare filaments with high flexibility and strength were also developed.

TABLE OF CONTENTS

1.162

and the second second

THE TREES AND TO A DESCRIPTION OF THE ADDRESS OF TH

				Page No.		
I.	INTRODUCTION					
II.	SUMMARY					
IXY	FUTURE WORK					
IV.	DISCUSSION OF WORK					
	<i>^</i> •	Tec	chnical Background and Approach	6		
	в.	Exp	perimental Procedures and Tests	7		
		1.	Preparation of Niobium Carbonitride Filament			
			Yarns from Carbon Precursor	7		
		2.	Preparation of Niobium Carbonitride Filament			
			from PN Precursor	9		
		з.	Fiber Characterization	11		
	c.	15				
		1.	General Considerations for the Chemical Conversion			
			Process	15		
		2.	Effect of Temperature Profile of Mullite Furnace			
			on the Fiber Composition	16		
		3.	Investigation of Furnacing	17		
		4,	Improvement in Mechanical Properties by Multi-step			
			Process	18		
		5.	Microscopic Examination	19		
		6.	Critical Current Measurement	20		
v.	REF	FERE	VCES	22		
VI.	TAP	BLES		24		
VII.	FIGURES					
VIII.	. APPENDIX					

iv

لمنفتحه

£5

and the second state of th

K-WIRHEAR D

		•	
j	an fan fan fan fan fan fan fan fan fan f		
		LIST OF TABLES	
			<u>Page No</u>
	1.	Products of the Reaction "C Fiber + $NbCl_5 + H_2 + N_2$ "	24
		Static Run	
	2.	Products of the Reaction C fiber + $NbCl_5 + H_2 + N_2$	25
		Continuous Run	
T	3.	Product: of the Reaction C(Fiber) + NbCl ₅ + H_2 + N_2	27
	4.	Continuous Reactions - Multiple Passes	28
	5.	Products of the Reaction BN (Fiber) + NbCl ₅ + H_2 + CH ₄	29
	6.	Effect of Heat Treatment on Structure of NbCN Fibers from	30
)) 1		BN Precursor	
!	7.	Critical Temperature Measurement of Some Superconductive	31
		Filament Yarns	
	8.	Critical Temperature Measurement at Various Magnetic	32
		Fields	
	9.	Critical Current Determination on Single Filament of	33
		Niobium Carbonitride	
	10.	Superconductive Properties of Some NbC_XN_{1-x} Yarn	34
		Determined at AFML	
	11.	Tensile Strength of Some NbC_XN_{1-X} Filaments	35

v

and the second se

LIST OF FIGURES

7. . .

٠.

		Page No.
1.	Schematic of Reactor for Preparation of NbCN Fibers	36
	from Carbon Yarn	
2.	Schematic of NbC ¹ 5 Vaporization Apparatus	37
з.	Typical X-ray Diffraction Patterns of Niobium Carbonitride	38
	Filament Yarns	
4.	Critical Field Measurement of B933-20-4	39
5.	Critical Field Measurement of B933-20-6A	40
6.	Critical Field Measurement of B933-20-6C	41
7.	Critical Field Measurement of B452-92-3	42
8.	Critical Field Measurement of B452-90-4	43
9.	Critical Field Measurement of B452-90-5	44
10.	Critical Field Measurement of B452-93-7	. 45
11.	Sample Test Configuration for Determination of T_c and J_c	46
12.	Electron Micrograph of the End View of B452-92-2 Niobium	47
	Carbonitride From Carbon Precursor Continuous Run	
13.	Electron Micrograph of Surface of B452-92-2 Niobium	48
	Carbonitride From Carbon Precursor Continuous Run	
14.	Electron Micrograph of End View of B452-93-7 Niobium	49
	Nitride from BN Precursor Continuous Run	
15.	Electron Micrograph of Surface of B452-93-7 Niobium	50
	Nitride from BN Precursor Continuous Run	
16.	Electron Micrograph of Niobium Carbonitride Fibers from	51
	Carbon Precursor by a Multi-Step Process	

LIST OF FIGURES Contd.

Page No.

The second s

THE REAL PROPERTY OF THE REAL

17.	Layer Structure of Niobium Carbonitride Fibers From	52
	Carbon Precursor Prepared by a Multi-Step Process	
18.	Surface Morphologic of Niobium Carbonitride Fibers	53
	From Carbon Precursor by a Multi-Step Process	
19.	Schematic Diagram of Modified Reactor for Preparing	54
	Superconductive Filaments	
20.	Reactor for Electrical Self Heating of Carbon Yarn	55

vii

SECTION I

INTRODUCTION

The need for a better continuous superconductive filamentary material has become more and more urgent in order to meet the demands for current and future applications. These include energy storage, rotating machines (motor and generator), ¬agneto hydrodynamic plasma confinement coils, propulsion motors, power transmission, magnetic ore separators, etc.

Since the early 1960's, the science and technology of superconductivity has attracted considerable attention. Much of the effort has been devoted to development of new superconducting alloys. Up to now, hundreds of alloys and numberous elements are known to be superconducting. A high field Nb₃Sn superconductor made by advanced vapor deposition techniques is now commercially available as a ribbon composite.¹ Fine and flexible wires of a Nb-Ti alloy have been drawn and produced commercially by metalurgical methods. Applications of these two materials are somewhat restricted because of their intrinsic properties and complicated manufacturing processes. It is clear that a significant advance of superconductivity technology still depends mainly upon major breakthroughs in materials development. It is, therefore, extremely important to develop a continuous superconducting filament yarn with fine diameter, high critical field, high critical temperature and high critical current. The fine diameter is particularly important because it reduces the temperature rise caused by flux jumps to a low and safe level and the ac loss due to the "intrinsic" magnetization.

Beginning July 1, 1971 a program on "Development on Process For

ł

Producing Continuous Fine Diameter Filaments of Superconductors" was initiated under funding from AFML. The objectives of the program were to:

ST. 2167.

MANPER IN

なんがください しまた ちょうてん しまた どうたいやく ちょうかい あたたいたいたまた かんたいたいちょう

- Develop various fiber compositions by the chemical conversion of fine diameter carbon and boron nitride fibers in order to establish preferred superconducting systems.
- 2. Develop continuous processes for converting the precursor fiber into the preferred system defined in "1" and to optimize the process with respect to the superconducting and mechanical properties of the continuous filament yarns.
- 3. Establish techniques for superconductivity measurements.
- 4. Establish correlations between process parameters, fiber morphologies and superconducting behaviour of the fiber.

Work in all these areas was carried out. Major efforts were placed on preparation of niohium carbonitride yarn from both carbon and buron nitride precursors. The superconductivity measurements were conducted at Cornell University under the direction of Dr. W. W. Webb. Results are discussed in the subsequent sections.

SECTION II

SUMMARY

A program to study the preparation of continuous fine diameter niobiumbase superconductive filaments by a chemical conversion method was initiated on July 1, 1971 under AFML support. Carbon and boron nitride filament yarn were used as the precursor and a mixture of niobium pentachloride, hydrogen and nitrogen was used as the reactant. Important process parameters affecting the composition and properties of superconductive filaments such as reaction temperature, contact time in the hot zone, composition of reactants, basic design of reaction chamber, temperature profiles of the furnace and the physical compactness of precursor yarn were investigated. During the first quarter efforts were placed on demonstrating the technical feasibility of the chemical conversion method for niobium carbonitride formation. In the second quarter, work was aimed at devising continuous processes for preparing the niobium carbonitride filaments from carbon and boron nitride precursors. During the remainder of the contract period, efforts were devoted to upgrading the mechanical properties of the fiber to improve the flexibility and to avoid fusion of filaments by modifying the reaction furnace and optimizing reaction conditions. The important accomplishments achieved during this first year's effort are summarized below:

A. The feasibility of preparing fine diameter niobium-base superconductive filaments by chemical conversion method was demonstrated. ないないというないないないないのできたのであっていたのであっていたのです。

B. A continuous process for converting carbon and boron nitride filament yarn into niobium carbonitride, NbC_xN_{1-x} , was developed.

-3-

- C. The conditions for preparing niobium carbonitride fiber with an optimum composition were defined.
- D. The procedures for characterizing the superconductive filaments were established.
- E. A process for producing flexible niobium carbonitride filament yarn was developed.
- F. Niobium carbonitride fibers from both carbon and boron nitride yarn with a critical temperature as high as 19.05 K were prepared. The critical current of some of the niobium carbonitride yarn was determined in the range of 0.4-1.0 $\times 10^5$ amps/cm².

ŧ

SECTICN III

FUTURE WORK

Future work will include the following areas:

Star - 20- - -

- Develop precursor fibers with finer diameters, 5,4 for carbon fibers and 4,4 for BN filaments.
- Continue developing processes for preparing superconductive niobium carbonitride filament yarns with improved mechanical properties.
- Produce continuous superconductive filament yarns in larger quantities for evaluation.
- 4. Develop techniques for coating the superconductive filaments.

SECTION IV

DISCUSSION OF WORK

A. Technical Background and Approach

The preparation of very fine filaments of ceramic and refractory materials has always been a challenging task. Conventional fiber forming techniques such as melt spinning, dry spinning, wet spinning and hot extrusion are not applicable due to the high melting point and unfavorable rheology of the melt. The fabrication of superconductive alloys into the fine diameter filaments encounters the very same problems.

The chemical conversion process developed at The Carborundum Company has proved to be a unique and powerful approach for making incrganic fibers which are impossible or extremely difficult to make otherwise.²⁻¹¹ The process involves converting an already available precursor fiber into another by virtue of chemical reactions. Thus, the difficult fiber forming task is eliminated. The fiber produced by this process retains the physical form of the starting material and usually displays good strength.

The preparation of niobium carbonitride fiber, NbC_XN_{1-X} , is accomplished by reacting carbon or boron nitride fiber with niobium pentachloride in the presence of hydrogen and nitrogen. The hydrogen acts as a reducing agent to reduce niobium pentachloride into niobium metal which, in turn, reacts with carbon and nitrogen to form carbide and nitride respectively. The following reaction sequence represent a simplified scheme for the conversion.

-6-

$$NbC1_{5} + H_{2} \longrightarrow Nb + HC1 \qquad (1)$$

$$Nb + C + N_{2} \longrightarrow NbC + NbN \qquad (2)$$

$$NbC + NbN \longrightarrow NbC_{x}N_{1-x} \qquad (3)$$

$$Nb + NbC_{x}N_{1-x} \xrightarrow{N_{2}} NbC_{y}N_{1-y} \qquad (4)$$

_ _ _ _ _ _ _ _ _ _ _ _ _

The degree of conversion of carbon into carbonitride phase depends upon the amount of niobium metal available. Too much Nb deposit (reaction 1) on the carbon filament usually causes fusion and yields a brittle fiber bundle. On the other hand, inadequate deposition will result in a fiber with a low degree of conversion. One way to solve this problem is to supply the niobium metal to the system by a stepwise manner. In fact, highly flexible niobium carbonitride filament yarns with a degree of conversion at the level of above 20% have been prepared by a multi-step process. Detailed discussion of experimental work will be given in the next section.

The conversion of boron nitride filaments into niobium carbonitride products likely follows a similar mechanism except the carbon source is supplied by the gas reactant such as methane or butane. The advantage of using boron nitride fiber as the precursor is the fine diameter of the fiber which is about 6μ . This facilitates the conversion and provides a more flexible filament.

- B. Experimental Procedures and Tests
 - Preparation of Niobium Carbonitride Filament Yarns from Carbon Precursor

The precursor used was a CY2-2 carbon yarn, a standard 2 ply continuous carbon yarn manufactured by The Carborundum Company. Prior to the reaction, the yarn was unplyed and untwisted to allow -7-

efficient contact between carbon and reactants. In the reaction, a single ply bundle which contains 720 filaments with an average filament diameter in the order of 10, was used. (In the second half of contract period a technique to produce a carbon yarn with an average filament diameter of about 7, was developed. This was accomplished by stretching the partially carbonized fiber under nitrogen atmosphere in a two-staged furnace, 700 °C and 2000 °C.) Very slight tension was applied to avoid sagging and to keep them parallel in the reactor.

The conversion reaction was carried out in a high temperature furnace. It was found that the outcome of the result depended very much upon the furnace configuration. This will be discussed in detail in the Section of IV C, Discussion of Results. Almost all the niobium carbonitride filament yarns produced were made in a Globar heated mullite furnace. A schematic reactor construction is shown in Figure 1. The protection tubes at both ends were used to control the reaction between the carbon yarn and the gas reactants, $NbCl_5$, H_2 and N_2 . The position of these tubes can be adjusted to optimize the conversion reaction. The niobium pentachloride was preheated in a silicone oil bath at \sim 200 °C and was admitted to the reaction chamber by passing a carrier gas of Ar or N₂, over the NbCl₅ surface. In Figure 2, a sketch of a NbCl₅ gas generator is shown. Initially, a number of static reactors were made varying reaction time, temperature and the composition of gaseous reactants which was accomplished by changing the flow rate of carrier gas over niobium pentachloride. The yarn to be converted was kept stationary during the reaction.

-8-

At the end of reaction, the reacted yarn was removed directly from the reaction zone for evaluation. It was found that the optimum reaction temperature was 1400-1500 °C. In most cases, fibers with a distinct two phase composition NbC-NbC_xN_{1-x} or NbC_xN_{1-x}-NBN were obtained. The results of static runs are summarized in Table 1.

The continuous process for preparing niobium carbonitride yarn was then developed using basically the same apparatus shown in Figures 1 and 2. A number of runs were made by varying temperature, contact time, flow rate of carrier gas, reactant composition, etc. It was found that the composition of the products was affected by the location of the protection tubes which controlled the reaction environment. Results of continuous runs are summarized in Tables 2 and 3. To improve fiber flexibility, a multi-step reaction process was developed. Fibers with good flexibility and various degrees of conversion were prepared. The results are shown in Table 4.

2. Preparation of Niobium Carbonitride Filament Yarns from BN Precursor

The preparation of niobium carbonitride filament yarn from boron nitride was also carried out. The precursor was a continuous BN filament (100 or 400 ends with an average filament diameter of the order of 6_{μ}). The conversion was achieved by the following reaction:

BN + NbCl₅ + H₂ $\xrightarrow{CH_4 \text{ or } C_4H_{10}}$ NbC_xN_{1-x} Methane or butane was used as the carbon source for the reaction. and the second secon

-9-

The reactor used was basically the same as that used for converting carbon fiber precursor. A number of runs were carried out with and without carbon yarn adjacent to the BN filaments. It was interesting to note that the presence of carbon yarn tends to regulate the carbon content of the product. In addition, the composition of niobium carbonitride filament produced was governed by two important parameters, the methane concentration level and the flow rate of argon carrier gas. The complete results are shown in Table 5. It was obvious that the carbon content increased with increase in methane flow rate and the presence of carbon yarn.

The x-ray patterns of the products were usually broad due to the presence of a wide range of compositions. The composition changed and the x-ray pattern sharpened as the sample was further heat treated at ~ 1500 °C. The effect of heat treatment is shown in Table 6. The data indicated that NbC_xN_{1-x} converted into NbN in the presence of BN core at 1500 °C.

Recently NbN filaments were prepared by reacting BN with "NbCl₅ + H_2 " in the absence of a carbon source (see B452-93-7 in Table 5). More work on this system will be explored in the future.

There are two major areas for improvements which should be accomplished to make the "BN route" attractive.

 Tight packing of filaments in the yarn will be eliminated to reduce difficulties in reactant penetration. This can be achieved when the quality or the precursor yarn is optimized.

2) The degree of conversion will be increased by adjust-

-10-

ing the reaction time and reactant concentrations.3. Fiber Characterization

1) X-ray Analysis

7, CHARAC (#1, R.)

The x-ray diffraction analysis was used routinely to characterize the structure of superconductive filaments produced from various runs. Since the lattice constants of niobium carbide (NbC_x) , niobium nitride (NbN_x) and niobium carbonitride (NbC_xN_{1-x}) are all known to depend upon the composition it is therefore possible to estimate the fiber composition from the x-ray data. This was actually done on a routine basis according to the procedure described below.

(1) Determination of Lattice Constant

The sample to be determined was mounted in a Debye-Scherrer Camera (114.6 mm) which was in turn mounted on a Phillips x-ray machine using Cu K_r radiation. Lattice constants of the fibers were then determined by analyzing the diffraction film. Good diffraction patterns were obtained under the conditions of 35 KV, 18 mA and three hours of exposure time. There was usually good resolution of the K_s and K_s lines in the back reflection which enabled one to make precise lattice constant calculations. Typical x-ray diffraction pattern of niobium carbonitride filaments are shown in Figure 3. The film was mounted on a film reader which reads 20 directly in millimeters with an error of ± 0.01 mm (± 0.01 °). The position of the 440 reflection which occurs around 160° (20) was measured and the lattice

and the second stranger with the second s

-11-

constant, a, was calculated from the following equation:

a = d
$$h^2 + k^2 + 1^2 = \frac{7}{2 \sin h^2 + k^2 + 1^2}$$

where $7 = 1.5405 \text{ A}$ (known)

h, k, l = Miller indexes (assigned)

O = diffraction angle (measured experimentally) (2) Composition Determination

Both NbC and NbN have a face center cubic crystal structure with lattice parameters of 4.470 A and 4.392 A respectively. The lattice constants of niobium carbonitrides lie somewhere in between depending upon the composition.^{12,13} It was also known that a number of carbon deficient miobium carbides and nitrogen deficient and rich niobium nitrides do exist and have lattice constants different from the stoichiometric carbide and nitride.¹⁴⁻²⁰ For the NbC system the lattice parameter increases from 4.437 A for NbC_{0.72} to 4.470 A for NbC_{1.0}. On the other hand the lattice parameter for NbN is highest for NbN_{1.0} at 4.392 and decreases to 4.381 A for NbN_{0.86} and 4.380 at NbN_{1.05}.^{18,19}

The relationship between the lattice constant and the composition can be summarized as follows:

System	Lattice Constant Range
NbC _X	4.437 A - 4.470 A
NbC _x N _{1-x}	4.392 A - 4.470 A
NDN _x	4.380 A - 4.392 A

With this background information on hand it is possi-

-12-

ble to estimate the fiber composition by x-ray with the following exceptions.

- (a) There is an uncertainty in structure $(NbC_x \text{ or } NbC_xN_{1-x})$ when the lattice constant falls in t: region of 4.437 A - 4.470 A.
- (b) There is an uncertainty in nitrogen content in NbN_{χ} (nitrogen rich or deficient) when the lattice constant is smaller than 4.392 A.

The uncertainty can usually be clarified by direct chemical analysis.

2) Superconductivity Measurements

Most of the superconductivity measurements were carried out at Cornell University under the direction of Dr. W. W. Webb who is the Technical Consultant for the contract. The procedures used for critical temperature, critical field and critical current measurements are described in the Appendix Section. Results of measurements are summarized in Tables 7 through 9 and Figures 4 to 10. Some measurements were also carried out at AFML and the procedures used are described below.

(1) Critical Temperature Measurement

Approximately 1.5 cm lengths of yarn were laid on 3/4" x 3/4" glass slides. Current leads (24 ga. copper wire) were connected to the yarn ends using Engelhard silver paint. Voltage leads were then attached to the sample in between the current leads. (See Figure 11)

-13-

The glass slide was then put on a circular copper block and kept in contact with it using grease and a piece of small metal bar (See Figure 11).

The second the sea when the

After the sample leads were connected to wires long enough to extend out of the Dewar flask, the sample was lowered to the Dewar.

The sample chamber was then filled with liquid helium. A small current, usually 1 ma, was then put through the sample. If the sample was a true superconductor there would be no voltage across the superconductor. In some cases there was a slight voltage, indicating a residual resistance. The sample was then allowed to warm up while temperature and voltage measurements were taken on a multi-point recorder. Auxiliary heaters were sometimes used to raise temperature at a faster rate. The transition temperature was determined by measuring the range in temperature over which a voltage appeared. For a sample with residual resistance the transition was determined by a sharp rise in voltage.

(2) Critical Current Measurement

Charles and the second state of the second sta

المتحافظ ومعموما أحوك الدهاك

The same sample and apparatus used for T_c is used here, except the current leads are connected to a higher capacity power supply. With the sample in liquid helium at 4.2°K and outside any magnetic field, an increasing current is passed through the sample. The voltage leads are connected to a Keithley nanovoltmeter set to detect

-14-

 $l_{\mu}V$ accorss the sample. The amount of current needed to produce $l_{\mu}V$ across the sample is taken to be the critical current, since it drives the sample normal.

3) Microscopic Examination

Scanning electron micrographs of a number of superconductive filaments were made at Carnegie-Mellon University and are shown in Figures 12 to 18. It will be shown later that the morphology of samples correlate well with the preparation conditions and the superconductive properties.

4) Mechanical Test

Tensile strength measurements were made for a small number of samples. The tests were carried out on an Instron machine using 1" as the gauge length. Results are shown in Table 11.

C. Discussion of Results

1. General Considerations for the Chemical Conversion Process

The preparation of fine diameter refractory fiber utilizes two basic concepts: use of available fiber as precursor to eliminate the fiber forming task and conversion of one fiber into another via chemical reaction. The method has been proven to be effective for many systems. It is important to realize, however, that there are theoretical and practical limitations in this method.

- 1) The desired fiber compositions must be thermodynamically feasible from the precursor and reactant.
- 2) Increase in reacted phase must be possible throughout

-15-

「ころうちょうないでのです」と、ないころのかいろうないで、ちょうちょうい

the conversion process. This is achieved by a diffusion process.

3) Since the conversion is a diffusion controlled process the rate of reaction is usually slow. Fine diameter precursor fibers are necessary.

All these considerations are applicable to the case of niobium carbonitride fiber preparation. The feasi/ility of the reaction was demonstrated by the analysis of reaction products from carbon and boron nitride precursors. The increase in degree of conversion is believed to be accomplished in a stepwise manner as indicated by a series of chemical reactions shown in Section IV A. The composition and properties of products are strongly affected by the process conditions which will be discussed in subsequent sections.

2. Effect of Temperature Profile of Mullite Furnace on the Fiber Composition

This discussion is related to the preparation of niobium carbonitride, NbC_xN_{1-x} , from a carbon precursor in a mullite reactor (See Figure 1). It was shown in the static runs (See Table 1) that all the samples produced displayed a distinct two phase composition. In these experiments, the reacted fibers were removed rapidly from the hot zone to the room environment. The sudden decrease in temperature served as a "quenching" which retained the meta stable niobium carbonitride structure. On the other hand, fibers produced from a series of continuous conversion experiments carried out in the first quarter did not show the distinct two-phase feature. The diffraction due to niobium

-16-

carbonitride phase was missing or extremely diffused and weak (See Table 2). In these experiments, the protection tubes were set 3" apart. As the niobium carbonitride fiber left the reaction zone it entered the protection tube in the outlet end and was cooled slowly in the absence of reactant mixtures. It was in this step that the niobium carbonitride decomposed into niobium carbide. The retention of the niobium carbonitride phase was made possible by increasing the separation between the protection tube to 6". The presence of reactant mixture, $NbCl_5$, H_2 and N_2 , in the cooling stage was sufficient to retain the carbonitride phase. Table 3 summarizes the results of continuous runs in this modified furnace configuration. The x-ray diffraction pattern of these samples was broad but the two-phase feature (NbC + NbC_xN_{1-x}) was definitely detectable. It is important to point out here that the retention of carbonitride phase is necessary in order to achieve a high critical temperature. The highest critical temperature obtained thus far is 19.05K.

3. Investigation of Furnacing

One of the important factors to the success of the chemical conversion process is the precise control of reaction temperature. This was recognized in the mullite tube reactor. The feature which the mullite reactor does not possess is the ability to quench the yarn temperature in a continuous manner. This can be remedied by the use of an infrared reflector furnace or an electrically self-heating method. In the case of the IR reflector furnace, the precursor (either carbon or boron nitride filament

-17-

yarn) is heated by the infrared radiation. The effectiveness of this process lies in the prevention of deposition of reactants on the quartz tube. Any deposition would tend to block the radiation and prevent the conversion reaction. Figure 19 shows the schematic diagram of the IR reactor. The electrical selfheating method makes use of electrical conductance of carbon filaments. The temperature of the carbon precursor is controlled by a powerstat. The furnace configuration is shown in Figure 20. Both these approaches have the capability of reducing the fiber temperature rapidly, and therefore are particularly suited for making niobium carbonitride fiber via a sudden quenching technique. Preliminary results showed both approaches to be encouraging but further cptimization is needed.

4. Improvement in Mechanical Properties by Multi-step Process

One of the problems encountered in the static and continuous runs was brittleness and lack of flexibility of the yarn bundle caused by fusion due to heavy Nb deposition. This problem was resolved by a multi-step process. In order to avoid fusion, proper interfilament openings during the reaction should be maintained. This was achieved by passing the yarn very rapidly through the Mullite reactor. To increase the degree of conversion the partially converted yarn was reacted repeatedly in the reactor. The niobium metal was supplied to the system in a stepwise manner to avoid heavy niobium build-up and ensure flexibility and strength of the fiber. The mechanical properties of fibers produced by this process are shown in Table 10. It is apparent that the

-18-

multi-step process provides an effective approach for preparing highly flexible superconductive fibers.

5. Microscopic Examination

Scanning electron micrographs of the samples were made at Carnegie-Mellon University. The fibers were immersed in liquid nitrogen for several minutes, then fractured under liquid nitrogen. Micrographs of fractured ends, cross sections, and lateral surfaces at various magnifications were obtained. Figures 12 and 13 show the end view and the surface of the niobium carbonitride prepared from carbon yarn. The crenulated shape of the fiber is due to the retention of geometry of original carbon precursor. Figures 14 and 15 show the details of filament tip and surface of a niobium nitride (NbN_{.89}) derived from boron nitride fiber. Again, the fibers retained the original circular shape of the BN precursor. All the specimens shown in Figures 12 through 15 were prepared from static and single step continuous runs. The specimens displayed two significant features:

- 1) Uniform and continuous conversion and
- 2) Spot fusion to cause brittleness of the fiber

Scanning electron micrographs of fiber prepared from a multi-step process, C265-13-6, were also taken. The cross sections show that the fibers are basically rectangular rather than round, and that the internal structure shows layering (See Figure 16). The appearance of the fractured layers suggests that the filaments consist of a homogeneous core surrounded by one or two layers of a rough coating. The central core appears

のないないないないので、ないないないないないないないないないないない

-19-

to be about 5 microns in diameter, with the external coating approximately 1 micron thick. The fluted shape seems to originate in the central core, with 8 flutes found on many of the fibers shown. The external coating is granular while the central core is finer grained. Figures 17 and 28 show the outer layer after removal of the inner core by the fracture process. The difference in the grain size in the core and outside layer suggests the feasibility to control this parameter by changing the passage rate during the conversion.

6. Critical Current Measurement

In the early stages of the contract period, critical current measurements were carried out for the yarn specimens from carbon and boron nitride precursor. The current, Ic, in the sample bundle was measured experimentally according to test procedures described in the Appendix Section. It was realized that the precise determination of I_c of the fiber bundle was complicated by the uncertainty of filaments in the bundle. The critical culrent density of the superconductive phase, J_c, was obtained by dividing I_c by the total area of the superconductive coating. This was done by 1) determination of average coating area of filaments with a Quantimet and 2) proper assumption of number of filaments in the bundle. The number of filaments was assumed to be 720 and 300 for carbon and boron nitride precursor respectively for calculation purposes. Because of the uncertainties involved in the test procedures the results obtained from the yarn specimens were considered to be unreliable.

-20-

The effort was then switched to the determination of critical current on the single filaments. The results are summarized in Table 9. It is significant to realize that the niobium carbonitride filaments prepared by the multi-step process possess a J_c value in the range of 0.4-1 x 10^5 amps/cm². The spread of J_c values observed in the determination was believed to be caused by any and/or the combination of the following factors:

(1) Inhomogeneity in superconductive composition.

(2) Ununiformity in thickness of superconducting coating.

(3) Variation in grain structure on the filament surface. All these differences are expected to be eliminated or reduced as the process parameters used in the chemical conversion are fully optimized and brought under complete control. This will be the major study area in the future.

SECTION V

REFERMINES

- B. W. Roberts, "Superconductive Materials and Some of Their Properties", National Bureau of Standards Tech. Note No. 408
- J. Economy, R. V. Anderson, "Properties and Uses of BN Fibers", Textile Res. J., No. 11, 994 (1966)
- J. Economy, R. V. Anderson, "BN Fibers", J. Pol. Sci. <u>C</u>, No. 19, 283 (1967)
- J. Economy, R. V. Anderson and D. T. Meloon, "Use of BN Fibers in Composites", SAMPE 10, B49 (1966)
- 5. J. Economy, R. V. Anderson, U. S. Patent 3,429,722 (1969)
- J. Economy, R. V. Anderson and V. I. Matkovich, "Preparation of BN Fibers", J. Pol. Sci. in publication.
- V. I. Matkovich and J. Economy, "Structure of BN", Amer. Cryst. Soc. Meeting, Buffalo, N.Y. (1968)
- 8. D. Beerntsen, J. Economy and W. D. Smith, "High Strength, High Modulus Inorganic Fibers", AFML-TR-66-298 Part I. Sept. 1966
- 9. D. Beerntsen, J. Economy and W. D. Smith, "High Strength, High Modulus Inorganic Fibers", AFML-TR-66-298 Part II. May 1968
- 10. J. H. Mason, J. Economy and W. D. Smith, "High Strength, High Modulus Inorganic Fibers", AFML-TR-66-298 Part III. May 1969
- 11. D. Beerntsen, W. D. Smith and J. Economy, "Properties of Boron Carbide Yarn Prepared from Carbon Yarn", J. Appl. Poly. Sci., No. 9 365-375 (1969)

12. P. Duwez, and F. Odell, J. Electrochem Soc., 97, 299 (1950)

-22-

13.	N. Pessal, R. E. Gold and H. A. Johansen, J. Phys. Chem. Solids,
	<u>29</u> , 19-38 (1968)
14.	E. K. Storms and N. H. Krikorian, J. Phys. Chem., <u>63</u> , 1747-9, (1959)
15.	B. K. Storms and N. H. Krikorian, J. Phys. Chem., <u>64</u> , 1471-7 (1960)
16.	A. L. Giorgi, E. G. Sklarz and T. C. Wallace, Proc. Brit. Ceram.
	Soc., <u>10</u> , 183-93 (1968)
17.	E. Rudy, Technical Report AFML-TR-65-2, Part V, (1969)
18.	G. Brauer and R. Esselborn, Z. Anorg. Chem., <u>309</u> , 151-170, (1961)
19.	G. Brauer and H. Kirner, Z. Anorg. Chem., <u>328</u> , 34-43, (1964)
20.	V. Ya Naumenko, Sov. Pow. Met. and Metal Cer., Oct. 1970, 799-801.

فاستلقلان أوراست

. Will A States and a state will be stated by the second second second second second second second second second

and the second with a subscription of the second

in the second from the

TABLE 1

and the second second

PRODUCTS OF THE REACTION

"C Fiber + NoCl₅ + H_2 + N_2 "

Static Run

Reaction			Results										
Run No.	Temp.	Time (Min)	Fiber Density	Fiber Cor	aposition Phase B								
<u> </u>		<u>Line II </u>		rnase A	Fliase b								
B933-20-4	1400	10	4.5	NbC.94	NbC.18N.82								
20-5	1400	15	5.5	NbC 94	NbC.27N.73								
20-6	1400	20	6.0	NbC-86	NbC.3N.7								
22-1	1500	3	-	NbC.93	NbC.4N.6								
22-2	1500	6	5.7	NbC.81 ^N .19	NDNX								
22-3	1500	10	6.5	NbC.72N.28	NbN1.00								
22-4	1500	15	6.8	NbC.59N.41	NDNX								
22-5	1500	20	7.4	NbC.70 ^N .30									
				<u>X-ray Results and Comments</u>		Wide variations of com	position from NbC, 9 to NbC,5N,5	One phase-sharp NDC og or NDC ogN of	Phase A - diffuse NPC	Phase B - diffuse and weak Phase A - diffuse who	Phase B - diffuse and weak One broad phase NhC	or NbC.6282N.3818	
---	--------------	---------------	---	-----------------------------------	--------------	----------------------------------	-------------------------------------	---	-----------------------	---	---	-------------------	---------
		-	is ictant	H2	ß	S S	Ç	ያ ያ	50	50	ß	50	
		es: 3")	er Gase	(uim)	100	01 01 02 01 02 01	5	100	100	100 100	100	100	
2	un	tion Tube	Othe Diluent	AF (CO	250	250 250	050	250	1	250 250	250	250	
n	Continuous R	etween Protec	of NbCl ₅ Flow Rate Of carrier	(cc/min)	50	50	50	50	50	50 100	150	200	
		Distance b	orization Carrier Gas	Used	Argon	Argon	Argon	Argon	Argon	Argon Argon	Argon	Argon	
			Vap NbCI5 Temp.*	(0°)	197 197	197	197	197	202	202 202	202	202	
			ion Yarn Speed	(iin/min)	0.6 0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	* +2 °C
			React Temp.		1300 1350	1400	1450	0051	1400	1400 1400	1400	1400	
			Sample No.	(C214)	6-1 6-5	6-2	2 4 4		8-1	8 = 2 - 3 - 3	8	8 - 5	

-

リマンないできたいいいがいていたいたからない

TAPLE 2

.

PRODUCTS OF THE REACTION

C Fiber + NbCl₅ + H_2 + N_2

-25-

TABLE 2 Contd.

-

ŝ

12

PRODUCTS OF THE REACTION

C Fiber + $NhCl_5$ + H_2 + N_2

Continuous Run

(Distance between Protection Tubes: 3")

		X-ray Results and Comments	Phase A - NbC 88. 98	One broad phase. NbC.82~.92	UNDC.8194.1906		One broad phase.~NbC.86	U NUC.85W.15	Wide range of composition	from NbC _{.82} to NbC _{.5} N.5 Phase A -~NbC.88 Phase B - weak and diffuse
	st at		50	50	ያ	50	50	5 O	50	50
Guse	Read	min)	50	100	150	400	250	250	250	250
Other	Diluent	(cc/	250	250	250	250	I	t	1	1
of NbC15	Flow Rate of carrier	(cc/min)	100	100	100	50	150	150	150	350
rization o	Carrier	Used	Argon	Argon	Argon	Argon	Argon	Argon	Argon	Argon
Vapo	NbC15 Temp *	() ()	207	207	207	197	202	202	202	202
	ion Yarn Sreed	(in/min)	0.6	1.0	0.6	0.6	1.0	0.6	0.6	0.3
	React	ູ່ວ	1400	1400	1400	1400	1400	1400	1400	1400
	Sample	(C214)	4-2	-92 4-1	4-3	6-6	9 - 3	9-4	1-6	9-5

* ±2°C

-

1.1

.

.

Products of the Reaction $C(!!iber) + NbCl_5 + H_2 + N_2$ (Distance between Protection Tubes: 6" apart)

	X-ray Results	11	1111	1111	Broad range of composition	l strong and broad, 2 mod. and broad	<pre>1 strong ~ NbC,8, 2 mod. and sharp, NbC,34N,66</pre>	l strong and broad, 2 mod. and broad	l v. strong, 2 v. weak and broad	<pre>1 v. strong ~ NbC_{.8}, v. weak and broad</pre>
N2 diluent	(cc/mir)	530	530	530	530	500	500	500	500	500
Ч	(cc/min)	50	ß	50	50	50	50	50	50	50
NZ Carrier	(cc/min)	100	100	100	100	100	100	100	50	50
Contact	(nin)	1.28	2.14	4.17	9.27	6.00	4.45	3.10	4.45	3.10
Tom:		1400	1400	1400	1400	1500	1500	1500	1500	1500
	Sample	R452-90-1	R452-90-2	DAF2-00-3	B452-90-4	B452-92-2*	B452-92-3*	B452-92-4*	B452=92=5*	B452-92-6*

* All these samples show a 2-phase x-ray pattern
Phase 1 corresponds to NbC_x
Phase 2 corresponds to NbC_xN_{1-x}

C. West

÷Χ

- ----

ł

•

States

1. 144.

1.131.31

MUNATER I

Continuous Reactions - Multiple Passes

Versu	<u>7147</u>			one phase NbC.90		A - broad & strong ~ NbC _{.8}	B = broad & wak		A - broad & strong ~NbC.78	B - broad & mod.		A - sharp & strong NDC.94 B - mod. & strong NDC.12 ^N .88
510W	· YAT	good	good	good	good	good		good	good		good	fair
Conversion	(R)	1 1 1	111	8*8	3.0	7.2		6 •6	6.9		I I I	18.4
N2		600	600	600	600	600		600	600		600	600
H2		1	30	29	22	20		19	20		30	30
Argon Carrier	CC	25	65	65	70	70		70	70		65	65
Residence Time	(urm)	1.4	0.9	4.8	6.0	1.4		1.4	1.4		0.9	5.0
Reaction Temp.		1500	1500	1300	1400	1400		1400	1400		1500	1500
Pass	No.	1)	2	E	1)	2		(3	<u>م</u>		ד)	(3
Sample	No.	C265	11-2				C265	12-1			C265	8#1

 CONTRACTOR

102

Hot Zone Length - 5 inches

-28-

Ç,

Products of the Reaction BN (Fiber) + NbCl₅ + H_2 + CH_4

Comments	<pre>- With C-yarn adjacent to BN yarn</pre>	<pre>- With C-yarn adjacent to BN yarn</pre>	- BN Yarn alone	. With C-ya n adjacent to BN yarn	- BN Yarr alone
Composition	NbC.22 ^N .67) NbC.85 ^N .15) NbC.93 ^N .07)	NbC.47N.53) NbC.51N.49) NbC.66N.34)	NbC.36N.64) NbC.43N.57) NbC.60N.40)	$NbC_{28}^{N}NbC_{14}^{N}$	NdN, 89
Lattice Parameter (A)	4.423 4.460 4.465	4.435 4.438 4.448	4.426 4.432 4.448	4.418 4.401	4.384
CH4 Flow (cc/min)	1.0 3.0	1.0 3.0	1.0 1.4 3.0	11	1
Ar Carrier (cc/min)	50 50 50	100 100	100 100 100	50	50
Contact Time (min)	2.80 2.80 2.80	2.80 2.80 2.80	2.80 2.80 2.80	4.11 9.53	2.80
Temp.	1500 1500 1500	1500 1500 1500	1500 1500 1500	1500 1500	1500
Sample	C214-29-1 C214-29-4 C214-29-2	C214-30-1 C214-30-3 C214-30-2	C214-31-1 C214-31-2 C214-31-3	B452-93-3*1 B452-93-4*1	B452-93-7*'2

2. 200 . 70.3

1250172

*1 - Small amount of isobutane used.

*2 - No carbon-containing gas added.

STALL ST

• • • • きだいき きってい しょうさい シート・ディー・ション・デー デー・デー

and the second state of the second second

-29-

A

brand Share and the second states

all takes

avt ++7 t

Effect of Heat Treatment on Structure of NbCN Fibers from BN Precursor

Composition	NbC.4N.6			- NUC.35N.7~.5		NhC 4 - N				DO TINON -	
X-ray Pattern	Broad	Broad)	Sl. Broad	Sl. Broad	Sl.Broad)	Sharn	Mod	Sharp)	Sharp)	Sharp)	Sharp)
Lattice Parameter	4.43 ± 0.01	4.44 ± 0.01	4.44 ± 0.01	4.42 ± 0.01	4.42 ± 0.01	4.403 ± 0.001	4.405 ± 0.003	4.393 ± 0.001	4.394 ± 0.001	4.394 ± 0.001	4.394 ± 0.001
Time, Hr.	ž	22	4	8	0.083	.25	.50	Ч	1	0	Ŋ
Tenp. °C	3	800	1200	1400	1500	1500	1500	1500	1500	1500	1500
Sample	C214-31-2	:	£	=	2	=	E	=		F	44

and a second second

ŧ

-30-

CRITICAL TEMPERATURE MEASUREMENT OF SOME SUPERCONDUCTIVE FILAMENT YARNS

		Criti	cal Temperatu	ures	
Sample	Composition	L1	Tm	Th	Rn (m./.cm)
B933-20-3	NbC _O , of				
	Ä	9.1	1	9.7	40
	B	9.1	1	9.5	11
	υ	9.1	1	10.0	2.3
B933-30-4	NbCO.96	6.1	1	7.3	47
B933-20-4	NbCo, 94 - NbCo, 1 RNo, 82	17.1	I	17.3	15
B933-33-3	NbCr. 992	10.9	1	11.2	18
B933-22-1	NbCo. 93-NbCo. 4No.6				2
	A	14.16	14.2	14.5	56
	£	13.7	13.7	14.6	41
	υ	13.6	13.6	14.2	22
B933-20-6	NbCO.86-NbCO.3NO.7			8 1 1	1
	Α	11.2	12.3	15.7	2.8
	υ	13.4	14.37	16.18	106
	Q	12.82	13.8	15.6	290
	ய	12.8	13.6	15.9	280
B933-22-4	NbCo.59N0.41-NbN1.0			6 6 7	
	A	13.38	13.42	13.45	80
	υ	13.42	14.0	14.44	1000

1.2.20

crafe

2. Strain

Critical Temperature Measurement at Various Magnetic Fields

Sample	Precursor	Composition	Field (KOe)	11 (⁰ K)	E of	ц Ж
B452-90-4	υ	$NPC_{x} + NPC_{x}N_{1-x}$	0	15.8 36.1		16.1 16.6
			53	11.2	12.5	13.1
			100	6.2	8.6	9.4
	ţ	NbC a + NbC 34N 66	0	15.5		15.8 16 6
B452-92-3	נ		C 1	16.2	11.7	12.5
			5 C C F	7.4 A	7.6	8.7
			2	16.05		16.2
B452-90-5	υ	$NPC_{8} + NPC_{XN} - x$	>	16.4		16.9
			53	11.5	12.7	13.3
			C	6-1/2		13-1/2
B452-93-3	BN	NbC.28 ^N .72	р Ч			4-1/2
			βĘ			4.2
				11.3	15.0	16.0
R452-93-7	BN	08. NdN	с Ц		7.6	<u></u> 8.5
			v C	2.2	11.0	11.3
B452-93-6	BN	NdN, 98	5 6	4	4.3	7.2
		;		10.5	12.7	15.4
B452-93-4	BN	NDC.14 ^M .86	ر م	4.3	7.4	10.1
				4,2	4.8	7.2
			0	ŋ	7.3	8.4
C214-30-1	BN	NDC.47N.53	65		4.2	
	i		0	10.3	10.5	11
C214-29-1	BN	NDC.334.67	65		4.2	

All and the second second

Sample	Magnetic Field	Current	J _c *1
	(KG)	(Amps)	(Amps/cm ²)
C265-13-6, 3rd pass	0	6 x 10 ⁻⁶	60
	10	1 x 10 ⁻⁶	10
C265-18-2, 2nd pass	0	15 x 10 ⁻⁶	150
	10	10 x 10 ⁻⁶	100
C265-18-2, 3rd pass	0	4.5 x 10 ⁻³	4.5×10^4
	10	4.0 x 10 ⁻³	4.0×10^4
C265-23-4, 2nd pass	0 5 25 0 (repeat)	10.4×10^{-3} 10.2×10^{-3} 6×10^{-3} (8×10^{-3}) (7×10^{-3})	$ \begin{array}{r} 1 \times 10^{5} \\ 1 \times 10^{5} \\ 6 \times 10^{4} \\ 7.5 \times 10^{4} \end{array} $
Airco Cryoconductor *2 (~7M)	0 25	8 x 10 ⁻³ 7 x 10 ⁻³	2.1×10^4 1.8 x 10 ⁴

Critical Current Determination on Single Filament of Niobium Carbonitride

* 1 Area estimated for superconductor phase: $10\mu^2$.

* 2 Ni-Ti wire produced by Airco.

TABLE 10

Superconductive Properties of Some NbC_XN_w Yarn Determined at AFML

	Comments	I I I	Residual resistance	f I I	1 1 1	Residual resistance	Residual resistance	No residual resistance	Residual resistance	Residual resistance	
	Ic (Amp)	0.1	1	0.15	0.018	1	ł	1 1	1 1	I I	ę
	808 8	17.5	18.5	19.09	17.6	19.1	19.0				
ы Ч	50%	17.1	18.3	19.05	17.2	18.7	18.4	~ 18.2	nsition	~ 18	
	10%	14.8	17.4	18.95	15.4	18.4	17.6	•	No tra	•	
	Composition	NDN.89	NbC.26 ^N .84	NbC,25 ^N .8.5	NbC.84 + NbC.13 ^N .87	NbC _. gN _{.1} + NbN _{1.07}	NbC,9 ^N ,1 + NbN1,08	NbC,933 + NbC,15N,85	NbC.89 + NbC.2 ^N .8	NbC _{.8} + NbC _x N _{1-x}	
	Precursor	BN	υ	υ	υ	υ	υ	U	υ	υ	
	Sample	B452-93-7	B265-23-4	C265-23-3	C265-23-7	C265-24-1	C265-24-2	C265-13-6	C265-18-2	C265~18~5	Norton VSF

Note: All the I_C measurements were carried out at 0 KOe.

The second s

-34-

Tensile Strength of Some NbC_XN_{1-X} Filaments

Sample	Tensile Strength (10 ³ psi)	Conversion (%)	т _с (К)
Carbon precursor	139	-	-
C265-13-6, 1st pass	68.1	8.0	-
C265-13-6, 2nd pass	71.3	20.8	-
C265-13-6, 3rd pass	71.0	26.1	18.2

A STRAIN MARCHINES & 20



FIG.I - SCHEMATIC OF REACTOR FOR PREPARATION OF NDCN FIBERS FROM CARBON YARN

52559278

لفد معمدهن مساحد معاد تقرع فترع فتد وكالتسوي فلالتدرير س





a. C265-13-6, "NbC.923 + NbC.15N.85" From Carbon Precursor



u. C214-30-1, "NbC.47N.53" From Boron Nitride Precursor

FIGURE 3 - Typical X-ray Diffraction Patterns of Niobium Carbonitride Filament Yarns











FIG.8 - CRITICAL FIELD MEASUREMENT OF B452-90-4





たちのうちになっていたいであるとうというでいたかいとうとうとう

FIG. 10-CRITICAL FIELD MEASUREMENT OF B452-93-7



FIG. 11-SAMPLE TEST CONFIGURATION FOR DETERMINATION OF TC AND JC



Electron Micrograph of the End View of B452-92-2 Niobium Carbonitride From Carbon Precursor

Continuous Run



FIGURE 13

Electron Micrograph of Surface of B452-92-2 Niobium Carbonitride from Carbon Precursor Continuous Run



FIGURE 14

Electron Micrograph of End View of B452-93-7 Niobium Nitride from BN Precursor Continuous Run





Reproduced from besi available copy.

FIGURE 16

Electron Micrograph of Niobium Carbonitride Fibers from Carbon Precursor By a Multi-Step Process





g

FIGURE 18

Surface Morphologic of Niobium Carbonitride Fibers from Carbon Precursor By a Multi-Step Process





APPENDIX

THE STREET OF STATES AND THE STREET AND STREET AS A STREET AS A

Summary of Methods for Determination of the Superconducting Properties of Niobium Carbonitride Filaments and Yarns Produced by the Carborundum Company at Cornell University By W. W. Webb

A. Introduction

Preliminary planning of evaluation procedures for niobium carbonitride filaments and yarns contemplated testing at extreme conditions. We visualized measurements of D.C. critical currents of the order of hundreds of amperes in magnetic fields of 100 KOe a: temperatures ranging toward 20 K as a screening procedure prior to more sophisticated tests in A.C. magnetic fields and with A.C. transport currents. Special apparatus had been designed and built that facilitated these relatively difficult measurements over the temperature range from 1.2 K to over 20 K. A description of this apparatus appears as Section C of this report.

Initial measurements of the resistive transitions of the yarns showed that yarns of niobium carbonitride with the expected high critical temperatures and reasonable critical fields had been achieved reproducibly at the Carborundum Company. The standard four terminal resistive transition measurements used for this screening employed the sophisticated apparatus described in Section C of this report. Some of the details of specimen preparation are also mentioned in Section B.

••56-

B. General Procedures

Our measurements of T_c employed a dewar insert designed for temperature control of about ±0.01 K up to about 30 K using a calibrated lithium fluoride dielectric thermometer free from magnetic field perturbations, a calibrated germanium resistance thermometer and provisions for calibration with respect to the helium gas thermometer. This thermometer is described by R. A. Brand, S. A. Letzring, H. S. Sack and W. W. Webb, Rev. Sci. Inst. <u>42</u>, 927 (1971). Temperatures reported should be valid to about ±0.05 K above 4.2 K. At the low measuring power of these experimen's there is no thermal equilibration problem especially with helium exchange gas in the specimen can. The superconducting transition was detected by observing the onset and rise of resistance using 0.1 microvolt detection sensitivity of a Keithley model 148 or 149 nanovoltmeter and one milliampere mcasuring current. Resistances were recorded continuously with an x-y recorder as a function of temperature, and the tabulation of T_{C} gives ranges of temperatures bounded by the onset of resistance at 10^{-4} ohm and the temperature for 99% completion of the transitions to the normal resistance.

Contact to all of the samples which consisted of bundles of many filaments was made by soldering onto a previously applied nickel plating (the plating was easily done using a standard commercial electroless solution). The nickel plating stiffened the bundles and improved their ruggedness, but the plating was thin enough (a few mile) that the filaments retained their visual forms. Samples were soldered at both ends to a glass-epoxy circuit board with

-57-

copper cladding cut away to form individual four terminal sample positions. The samples were about 1-1/2 cm long with a gauge section (between voltage probes) of about 1 cm.

Critical temperature measurements in applied fields of about 50 and 100 kilogauss were also carried out in the same apparatus. In these experiments the transitions were found to be broad and "spikey" suggesting some sort of inhomogeneities that might suggest critical current limitations. Shapes of the $\frac{1}{2}$.C. I-V characteristic of the transitions were recorded and reported to show these effects.

Critical current measurements on yarns at 4.2 K and fields up to 100 KOe at a temperature of 4.2 K in the same apparatus confirmed the above concern. To avoid destroying these short samples by explosive heating at the normal transition protective brass shunts were used. Repetition of the transitions without brass shunts showed that a resistive component appeared in the nominally superconducting yarns at rather low currents suggesting even greater inhomogeneities. Rather brittle mechanical properties made the measurements quite tedious.

Because of these problems the focus of the testing shifted to single filament samples extracted from yarns. Long samples were contemplated to avoid contact problems which were imagined to be a possible cource of small critical currents. However failure of protracted effort made it very clear that the lack of mechanical ruggedness of these filaments made this approach impractical. Measurement methods were then restricted to simple, entirely standard, four terminal resistive transition observations on short (1 cm) single filaments. Ecth silver paint and solder terminals were used

-58-

and it was very clear that significant voltages (microvolts) appeared at very low currents (~10 milliamps). The mechanical apparatus for these experiments was a simple, standard "namy down" dipped into liquid helium in a 4 KOe superconducting magnet. Measurement techniques were the same as those used in the more elaborate apparatus. The contacts were generally silver paint but since the critical currents are small and the speciments. Several precision low current power supplies have been used to provide the transport current and continuous copper wire leads (no plues) from helium temperature to the Keithley nanovoltmeter to reduce thermal EMF's to < 0.1 μ V.

C. Experimental Apparatus

125

and a start of the second start of the second start of the start of the second start of the second start of the

Two magnets were used in this work: a 40 KOe Nb-Zr superconducting solenoid for low field work, and a 100 KOe Nb₃Sn magnet. Both were homogenous ($\sim 1/2\%$) over the 1-1/2 inch diameter and over a 2 inch length. The low field magnet was driven by a ramping power source described before⁽¹⁾ or by programming a commercial low voltage power supply. The 100 KOe magnet was driven by a superconducting flux pump.

An insert cryostat was fabricated which could be used in either magnet. The cryostat was formed by a copper sample chamber mounted inside but thermally isolated from an outer stainless steel chamber. The design of the cryostat is shown in Fig. 1. The respective bulkheads for the two chambers (detailed in Fig. 2) were joined by the stainless tubes used for electrical interconnections and plumbing. They were hydrogen brazed in place. The copper and stainless shells

-59-

were attached and sealed to these flanges by #4-40 screws and indium O-rings. A copper plate for holding electrical connections, heaters, etc. was mounted beneath the copper bulkhead (Fig. 1). To this could be attached different sample holders. This provided a small temperature controlled volume in the center of the field in which the samples were mounted. Liquid helium could be admitted to the chamber by an external valve and pumped on to reduce the temperature. A stainless steel Hoke valve was used, with the stem lubricated with molybdenum disulfide. The vapor pressure was monitored by a separate manometer tube (not shown).

יצע מולע מערים אינוי יובים אייניי כי באריוניוני<u>ו אי</u>

Electrical connections were made by sealing the wires with Stycast epoxy in small separate copper pieces which were then soldered to the bulkheads with low temperature solder (Indalloy #13, m.p. 125C; or Woods metal). These are shown in Fig. 2.

For general low current service connections, 16 pairs of Evenohm wire were sealed at the copper bulkhead (which also served as a heatsink to the inside chamber), heat sunk in the vacuum space to the outer wall at 4.2 K and connected at room temperature by a epoxy sealed connector on the vacuum line.

Current connections were made by fabricating a Nb_3Sn feedthrough of nine separate leads using special ribbon provided by General Electric. This ribbon had no copper stabilization so that it provided an effective thermal impedance between the inner chamber and the surrounding liquid helium (magnet) bath. An initial feedthrough using a single Nb₃Sn ribbon for each lead failed because a flux jump in the ribbon at 30A caused it to disintegrate in the vacuum space.

-60-
This problem was solved in part by using four ribbons in parallel for each lead. The ribbons were soldered to copper wires which were then sealed into a stainless steel tube with brass ends. The leads were insulated with fiberglass tape. This was soldered as a unit to the bulkheads, the tube protecting the rather fragile ribbons from subsequent damage. It was found that by orienting the tube so that the magnet fringe field was parallel to the Nb₃Sn ribbon surface, the remaining flux jumping was eliminated. The samples were connected to the feedthrough by commercial RCA Nb₃Sn ribbons soldered at each end. Eight twisted pairs of insulated brass wire sealed in a separate tube were used for voltage leads.

Both current and voltage leads were connected to switch outside the cryostat in the superconducting magnet helium bath as shown in Fig. 1. This was fabricated from several decks taken from (L&N) low thermal rotary switches. The current sections and contact were gold plated over the as-received silver alloy to eliminate the dielectric oxide coating which became very resistive at helium temperatures.

An extra deck on the current section of the switch placed a brass shunt of a few hilliohms in parallel with the samples and feedthrough. The resistance of the shunt was so proportioned that little current (< 1%) flowed in the shunt unless the superconducting feedthrough quenched, but when it did the current was diverted into the shunt thus protecting the Nb₃Sn ribbons from excessive heating. With this shunt, no further feedthrough failures were experienced. The shunt was removed for low current critical temperature and field measurements.

-61-

the state of the second second war

The voltage was measured on a Keithley nanovoltmeter at a full scale sensitivity of 1 V. The current was provided by ramping a programmable power supply with a maximum current of 100 A and monitored by a series shunt. These were recorded on an x-y plotter. The critical current electronics are shown in Fig. 3.

A DATE OF THE OWNER OF THE

A. 7. Mary ... Mrs. 29 4.50

The temperature was measured by a KCl:Li dielectric thermometer which, although requiring recalibration due to aging at room temperature, is insensitive to magnetic fields. This thermometer, developed by the author, has been the subject of a previous $paper^{(2)}$ and so will not be discussed further. The thermometer was used with an A.C. bridge as is shown in Fig. 4, using a precision (~0.1 ppm) inductive divider and phase sensitive detector. The reference capacitance used was a commercial silver-mica capacitor which was held in a small vacuum can and placed in a liquid nitrogen bath. The thermometer was calibrated against helium vapor pressure and a calibrated germanium thermometer. Connections to the dielectric thermometer were made through coaxial feedthrus constructed with ultra-miniature coaxial connectors (Microdot Lepra Con) again sealed in epoxy.

The temperature was regulated above 4.2 K by controlling a heater power supply with the bridge output. Below 4.2 K, additionally the pumping rate was controlled with a rubber manostat pressure regulator. The temperature was controlled and known to ± 10 mK at low temperatures and ± 20 mK at higher temperatures.

 (1) W. A. Fietz, Rev. Sci. Inst. <u>36</u>, 1306 (1965); and <u>36</u>, 1621 (1965).
(2) R. A. Brand, S. A. Letzring, H. S. Sack and W. W. Webb, Rev. Sci. Inst. <u>42</u>, 927 (1971).

-62-





-64-



Two samples could be accomodated, and the current and voltage leads were choosen by a multiple deck rotary switch Critical current electronics. in the helium bath. Figure 3.

and a stand and a standard at the second and the second and the second and the second at the second

-65-





;

-66-

SUPPLEMENTARY

INFORMATION

سند د ۸۰۰۰ می د ۲۰۰ کو د ۲۰۰ <u>کو کو کو د</u> می محمد ۲۰

ころいい きかんのかん かみこうい



DEPARTMENT OF THE AIR FORCE

WRIGHT LABORATORY (AFSG) WRIGHT-PATTERSON AIR FORCE BASL, OHIO 45433-6543

ERRATA

1/2.4/91

2

WL/ISL/M. Kline

Possible Missing Page to AFML-TR-72-189 (AD751545)

AD-751 54

ころろう いちかん ちょうちょう あんかいろう ちょうちょう しょう

٩,

FDAC Cameron Station Alexandria, VA 22304-6145

The attached page was missing from the above report (microfiche copy) Please check your files. Thank you very much.

MARTHA KLINE

Library Technician WL Technical Library Atch Pg 16