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Progress Report

MASTER

LASL Nb_3Ge Conductor Development

January 1—March 31, 1979

University of California

LOS ALAMOS SCIENTIFIC LABORATORY

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Compiled by

M. P. Maley

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Eleventh Quarterly Progress Report

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M. P. Maley

ABSTRACT

The eleventh quarterly progress report of the Los Alamos Scientific Laboratory program to develop Nb_3Ge as a superconductor with potential applications to superconducting power transmission lines covers the period January 1 - March 31, 1979. This is the first report of Phase III, which has as its goal the fabrication and testing of a 1.0-m length of coaxial cable using Nb_3Ge conductors. The technical program plan for meeting this goal is outlined. Modifications and repairs on the long sample CVD apparatus were completed and are described. Several tape sections coated in the apparatus were tested and used to define optimum process variables for producing Nb_3Ge with the best superconducting properties. Bend tests also were commenced to determine a minimum bending diameter for our tapes.

I. INTRODUCTION

The Nb_3Ge conductor development program of Los Alamos Scientific Laboratory (LASL) commenced a third phase on January 1, 1979. The long-term objective of the program is to develop a conductor suitable for application to superconducting power transmission lines (SPTLs) that is significantly superior to presently available conductors. More specifically, the aim is to exploit the record-high T_c (∿23 K) of Nb_3Ge to permit operation of a SPTL in the temperature range 14-16 K. In the initial phase of the program, completed in June 1976, we developed a chemical vapor deposition (CVD) process by which short samples of Nb_3Ge could be produced with superconducting properties that meet the requirements for power transmission at T = 12 K. A description of the program accomplishments through June 30, 1976 may be found in the EPRI Final Report (TD-200).[1] The second phase, begun on July 1, 1976, concentrated on the task of modifying the basic CVD process to produce long lengths of Nb_3Ge-clad tapes with material properties matching those of our best short samples. The effort culminated in the production of a 20-m-long Nb_3Ge-clad tape. The tape consisted of a 0.64-cm-wide x 25-μm-thick copper substrate, coated uniformly with a 4.0 μm-thick layer of Nb_3Ge. Sections taken from both ends of the tape had measured values for J_c of 2.5 and 2.4 x 10^6 A/cm^2 at 13.8 K and material parameters that varied by less than 5%. Phase II was completed on June 30, 1978 and is fully described in the EPRI Final Report EL-965,[2] entitled "Development of Nb_3Ge for Power Transmission Applications." Phase III, for which this is the first quarterly report, is aimed at the fabrication and testing of two 1-m sections of ac-SPTL using the long Nb_3Ge-clad tapes developed in Phase II.

This report covers the period January 1 - March 31, 1979 and is the eleventh quarterly report issued since the beginning of the EPRI sponsorship. In keeping with previous convention, we will refer to this report hereafter as PR-11. During the beginning of this quarter we established a preliminary technical program plan designed to lead to the fabrication and testing of the first cable section. Because we plan to test the first cable section at Brookhaven National Laboratory (BNL), consultation with members of the BNL-SPTL staff was carried out to ensure compatibility of our cable with their measurement apparatus. The form of our program plan following these discussions is outlined in Sec. II. The major effort during this quarter was devoted to restoring our Nb_3Ge-tape coater to operating condition. Following a period of six months during which the apparatus was not operated, considerable corrosion damage to the CVD coating system was discovered. Required repairs and modifications to the apparatus are described in Sec. III-1. Although operation was restored expeditiously, we discovered that some of the modifications have altered coating conditions sufficiently to require a readjustment of process variables to produce material with optimum superconducting properties. This effort, nearing completion, is described in Sec. III-2. In Sec. IV we discuss the results of critical current and bend tests which we have begun during the quarter.

During the next quarter we plan to produce the tape required for our first cable section and to fabricate the cable.

II. TECHNICAL PROGRAM PLAN

The tasks to be performed can be conveniently divided into two categories: conductor production and fabrication and test cable fabrication.

1. <u>Conductor Production and Fabrication</u>

   a. process optimization - A "fine tuning" of process variables will be carried out to ensure optimum superconducting properties and material reproducibility for the production of the tapes to be used in the cable. Critical current density (J_c) and T_c measurements will be the primary diagnostics.

   b. Substrate Selection - Prior studies have shown the importance of matching the coefficient of thermal expansion (CTE) of the substrate to that of Nb_3Ge. Equally important, however, is that the tape be capable of being wrapped around the 2.6-cm-diam mandrel for the inner conductor of the cable. Bend tests will be performed for tapes on the substrate candidates to determine minimum bend diameters. For the first cable, copper and copper-clad stainless steel are the two prime candidates. On the basis of the results of the bend tests, a substrate will be selected for the tape production.

   c. Tape Coating and Testing - The continuous coating CVD apparatus will be used to coat 4-6 μm thickness of Nb_3Ge on the substrate selected in step b. The tapes will be 0.64-cm wide by 25-μm-thick by 20-m long. Sections taken from the beginning and end of each tape will be tested for critical current I_c. A minimum standard I_c value of 800 A at 13.8 K will be required for both sections for the tapes used in the cable construction. A sufficient quantity of tape meeting this specification then will be produced.

d. Copper Electroplating of Tapes - The selected tapes will be electroplated with a thin flash (1-3 μm) of copper by the process described in EPRI EL-965[2]. The tapes then will be run back through the CVD apparatus in an inert atmosphere at 500°C in order to form a good bond of the copper to the Nb_3Ge surface.

e. Copper Stabilization - Additional copper (25 μm) will be added to each side of the tape in order to stabilize against flux jumps. This copper will be added either by soldering or by electroplating. The method selected will depend upon the results of bend tests performed on tapes stabilized by both methods.

2. Test Cable Fabrication

a. Mandrels and Jigs - A mandrel, 2.6-cm-o.d. x 1.0-m-long will be selected for the center structure of the cable. This size was chosen to be compatible with the output terminations of the BNL transformer. Jigs will be constructed for holding spools of tape for winding at the proper angle onto the mandrel.

b. Inner Layer Winding - Two layers of Nb_3Ge tape will be wrapped in a helical manner onto the mandrel at an angle near 45°. The wrap angle will be adjusted to ensure complete coverage for each layer with minimum butt-gap spaces. The two layers will be wrapped with opposite pitch. Copper rings will be soldered on top of the two layers for current connection on the input end and for shorting to the outer layers at the far end.

c. Placement of Probes and Instrumentation - A number of voltage and current probes will be installed along the inner conductor for the measurement of ac-losses. The exact configuration and placement of these probes will be determined after consultation with the BNL group.

d. Insulation and Outer Layer Winding - A thin layer of insulating tape will be applied followed by the outer two layers of Nb_3Ge-clad tape wound in the same manner as the inner two layers of the coax. The two layers will be shorted to the same copper ring at the far end and a third copper ring will be soldered to the outer layers at the input end for connection to the transformer.

It is expected that the tasks listed above will be completed by the end of June 1979. Testing of this cable is planned to be performed at BNL in the fall of 1979.

III. CVD-APPARATUS

The basic configuration of the CVD apparatus is shown in Figs. 2-5 and 2-11 of EPRI EL-965[2]. The work done in May and June of 1978 on the Nb-Ge-Ga ternary resulted in contamination of much of the system with galium chlorides, and the extended period from June to January without operation resulted in considerable damage to the apparatus from corrosion. Several components and a great deal of plumbing required replacement or extensive repair. This opportunity was used to replace the liquid $GeCl_4$ bubbler by a germanium chlorinator. It is hoped that this will improve the stability of operation as well as the material reproducibility. This system has the added advantage that the possibility of picking up impurities during the fractional distillation of liquid $GeCl_4$ is now eliminated. This, combined with a new source of Cl_2 (ultra high purity), is expected to make a product with fewer impurities.

Adding germanium chlorination does not in itself seem to have created any new problems. Chlorination is carried out at 320° C, as suggested by Braginski et al.,[3] and seems to proceed quantitatively to $GeCl_4$. The major problems encountered are related to deposition rate and the exact location of the sharp peak in the current density with Nb_5Ge_3 content.[2] Initial runs with the rebuilt system and the new germanium chlorination produced deposits which were ∿15% thinner than expected. Second-phase Nb_5Ge_3 contents and lattice spacings as a function of chlorine flow in the $GeCl_4$ system are shown in Fig. 1. The average lattice spacing observed is exactly the expected value for a deposition temperature T_D of 875 C; however, the variation of Nb_5Ge_3 content with chlorine flow has an unusual shape. Subsequent runs showed a continuing decrease in deposition rate, although composition was not altered significantly. Disassembly of the mixer preheater disclosed that an inordinately large amount of $NbCl_3$ was being deposited in this region because of the presence of gas baffles. These were removed and two more runs made with the the results shown in Fig. 2. Thicknesses still run from 5-15%

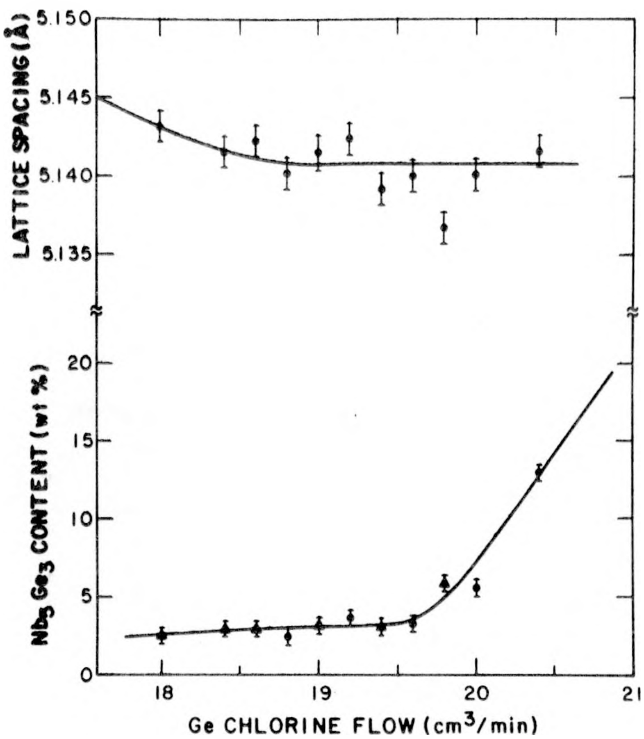

Fig. 1.
Second-phase Nb_5Ge_3 content (bottom) and lattice spacing of Nb_3Ge material (top), both plotted as functions of chlorine flow in the $GeCl_4$ system before removal of gas baffles from the mixer-preheater.

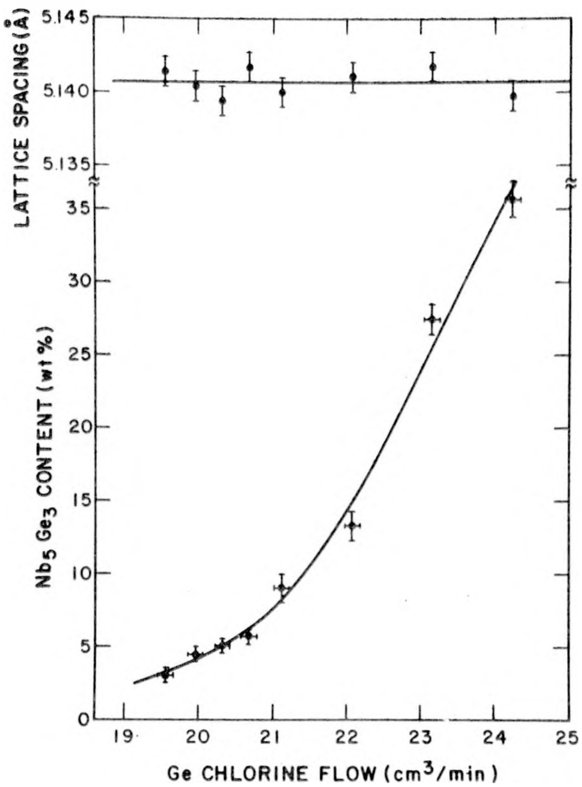

Fig. 2.
Second-phase Nb_5Ge_3 content (bottom) and lattice spacing of Nb_3Ge material (top), both plotted as functions of chlorine flow in the $GeCl_4$ system after removal of gas baffles from the mixer-preheater.

too thin, but the variation of Nb_5Ge_3 content with Cl_2 flow is now as expected. The lattice spacing remains at the correct value.

The problems described concerning deposit thickness caused sufficient concern to prompt us to run a test of germanium chlorination to determine if it was indeed quantitative. Three sections were deposited at identical Cl_2 flows and at argon carrier flows of 150, 100, and 50 cm^3/min. This range varies the salt dilution in the chlorinator by 300% and also changes the gas residence time by the same amount. If the chlorination were not quantitative, the amount of germanium transported would change significantly for these runs, resulting in changes in the Nb_5Ge_3 content of the deposit. The Nb_5Ge_3 concentrations in the three samples were respectively 2.6, 2.6, and 2.1 wt%, indicating no effect of the chlorination. These results confirm the observation by Braginski et al[3] that the chlorination is quantitative at 320°C.

IV. CRITICAL CURRENT MEASUREMENTS AND BEND TESTS

Critical current measurements were carried out on seven samples this quarter. These measurements were used as diagnostics and as a calibration of process parameters in the rebuilt and modified apparatus. One sample was measured before and after bending around mandrels of 2.5- and 3.8-cm-diam, the beginning of a study of minimum bending diameters for our tapes. The measurements were performed by the standard four-probe technique[2] over the temperature range 13.8-19.4 K in liquid hydrogen. All of the samples tested this quarter were 4- to 6-μm-thick coatings of Nb_3Ge on 0.64-cm-wide, 25-μm-thick copper substrates, which were pulled through the CVD-coating chamber. Critical current densities were determined by dividing I_c by the cross-sectional area of the Nb_3Ge. Measurements of thickness are no longer performed by metallography. A section of coated tape is measured and weighed along with a section of uncoated substrate. The Nb_3Ge thickness is then calculated from the x-ray density of the material (8.6 g/cm^3). This technique is estimated to be accurate to ±5%, where the metallographic technique was judged to be accurate to ±7-8%. The new technique requires about 5 min/sample, whereas metallographic examination required 30-45 min/sample.

The samples measured this quarter were all deposited at T_D = 875°C. A plot of I_c versus T^2 is shown for a typical sample in Fig. 3. As discussed previously,[2] the expression $I_c(T) = I_c(o)\,[1-(T/T_c{*})^2]$ generally gives a good fit to the data over a large range of temperature, excluding the region of the high-temperature "tail" above T_c^*. The value of T_c^* is generally 3-4 K less than the inductively measured value of T_c. All of the samples measured had values of $18.2 \leq T_c^* \leq 19.0$ K, in keeping with previous observations[2] at T_D = 875°C.

A summary of determinations of J_c (13.8 K) from these measurements is shown in Fig. 4. J_c (13.8 K) is plotted as a function of Nb_5Ge_3 content. The values of J_c (13.8 K) shown here are considerably below the

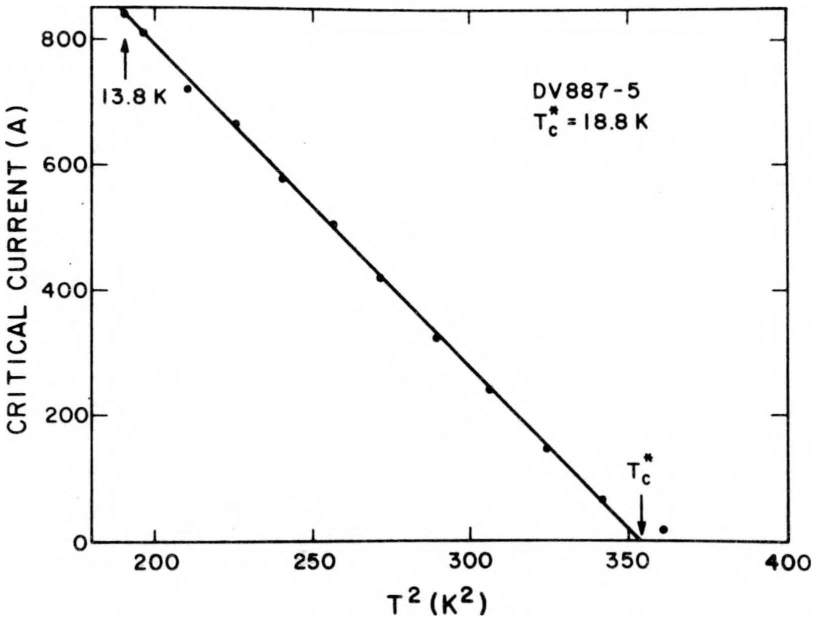

Fig. 3.
Critical current I_c versus T^2 for sample DV887-5 over the range $13.8 \leqslant T \leqslant 19.4$ K.

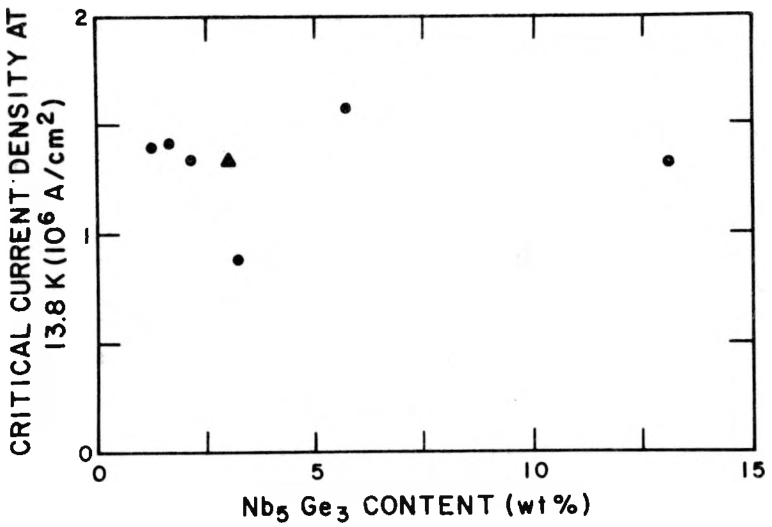

Fig. 4.
Critical current density J_c (13.8 K) plotted as a function of Nb_5Ge_3 content for Nb_3Ge-clad tapes coated in the rebuilt CVD apparatus.

peak values measured previously[2] at this temperature ($\sim$2.4 x 10^6 A/cm^2). Further investigations will be required to determine the cause of this discrepancy between the results in the old and the new apparatus.

In Fig. 5 we show the results of our first bend test as determined by I_c vs T measurements. The I_c vs T curve was first measured in the usual manner. The sample then was bent around a 3.8-cm-diam mandrel and remeasured. The process was repeated after bending around a 2.5-cm-diam bend.

The maximum strain in a flat ribbon of thickness t bent in a circular arc of diameter D is simply $\varepsilon = t/D$ %. For our estimated tape thickness, the bend at D = 3.8 cm should have caused slightly less than 0.1 % maximum strain. It is generally accepted that a tensile strain $\sim$0.1-0.2 % is sufficient to cause fracture in most brittle A-15 materials. The degradation seen here for $\varepsilon \sim 0.1$ % seems somewhat high. Further studies will need to be performed. For the cable fabrication to be successful, we must wrap the tape in a 45°-helix about a 2.5-cm-diam mandrel without damage. The radius of curvature ρ at a helix of pitch angle α and radius R is given by $\rho = R/\cos^2 \alpha$. For $\alpha = 45$, this gives $\rho = 2R$ and implies that wrapping our tape in a 45°-helix around a mandrel of diameter 2.5 cm will give a strain equivalent to a straight wrap around a 5.0-cm-diam. Inclusion of a prudent safety factor of

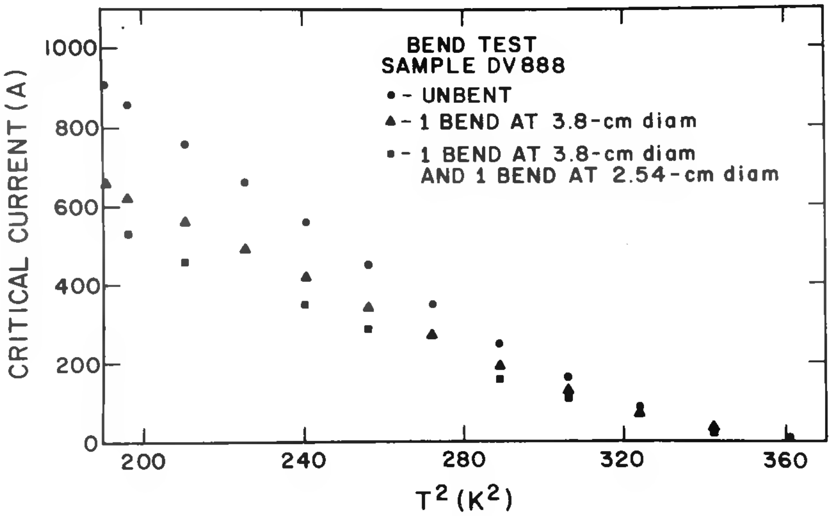

Fig. 5.
Critical current I_c versus T^2 for sample DV888; ● - as prepared ▲ - after bending around a 3.8-cm-diam mandrel, and ■- after subsequent bending around a 2.5-cm-diam mandrel.

two would indicate that we should design a conductor which will take a straight bend around a 2.5-cm diameter without degradation. Further tests of Nb_3Ge deposited on copper substrates will be required to determine a minimum-bend radius for the conductor. In addition we have arranged with J. Ekin to have three samples measured for critical current in a straight tensile-test rig at NBS-Boulder. If the results for copper substrates continue to give poor results, we will consider the Cu-clad stainless steel substrate for our first cable conductor.

V. PERSONNEL

L. R. Newkirk and F. A. Valencia are responsible for development and testing of the conductor, M. P. Maley and J. D. Thompson for ac-loss measurements and cable fabrication, and R. J. Bartlett and R. V. Carlson for critical current and bend test measurements.

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