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Progress Report

MASTER

LASL Nb_3Ge Conductor Development

January 1—March 31, 1980

University of California

LOS ALAMOS SCIENTIFIC LABORATORY
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Compiled by

M. P. Maley

LASL Nb_3Ge CONDUCTOR DEVELOPMENT
January 1 - March 31, 1980
Fifteenth Quarterly Progress Report

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ABSTRACT

The fifteenth quarterly progress report of the Los Alamos Scientific Laboratory program to develop Nb_3Ge as a superconductor with potential applications to power transmission lines covers the period January 1 - March 31, 1980. During this quarter, additional instrumentation was installed on our first 1-m Nb_3Ge cable in preparation for tests, which are now scheduled for May 1980. We succeeded in preparing three $Nb_3(Ge_{1-x}Ga_x)$pseudobinary compounds with compositions approaching the proper stoichiometry and with x = 0.08, 0.12, and 0.15, respectively. The replacement of germanium by gallium causes a slight depression ($\sim$1.0 K) of T_c and does not appear to influence H_{c_2} significantly. A microscopic examination of the edge material on sections of our Nb_3Ge-clad tape revealed longitudinal cracks extending along the edges of tapes with Nb_3Ge thickness $t \geq 4.0$ µm. Tapes with t = 3.0 µm show no evidence of such cracks, corroborating conclusions reached by ac loss measurements. The two layers of the inner conductor of our first 1-m test cable were wound with tapes coated with 4-6 µm of Nb_3Ge and are expected to contain longitudinal cracks. The two layers of the outer conductor of this coaxial cable were fabricated from tapes coated with $\sim$ 3.0 µm of Nb_3Ge and should exhibit lower ac losses.

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 ($\sim$ 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 fifth 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, 1980 and is the fifteenth quarterly report issued since the beginning of the EPRI sponsorship. In keeping with previous convention, we will refer to this report hereafter as PR-15.

We had planned to conduct tests on our first Nb_3Ge cable at Brookhaven National Laboratory (BNL) during this quarter. Unfortunately further delays in the BNL testing schedule have postponed our cable tests into May 1980. The fabrication of our test cable was completed in July 1979 and the first tests were originally planned for the period August-November 1979. Additional instrumentation was installed on our cable during a visit by J. D. Thompson to BNL in January. These modifications and other details concerning the planned tests at BNL are presented in Sec. II of this report. As discussed in PR-14, the delays at BNL have caused us to rearrange our program plan to concentrate on materials development during this period. The efforts in third element additions to Nb_3Ge and in lowering ac losses in our tapes have been continued during this quarter.

In PR-14 we described the first stage of our attempts to prepare stoichiometric $Nb_3(Ge,Ga)$ compounds. The aim of this program is to investigate the effect of substituting gallium for germanium on the stability of the A-15 lattice and upon such physical properties as T_c and the upper critical field H_{c_2}. Previous attempts to study the influence of ternary additions to Nb_3Ge have failed due to inability to achieve stoichiometry in the A-15 lattice. During this quarter we have succeeded in preparing three samples of near stoichiometric $Nb_3(Ge,Ga)$ with Ga to (Ga + Ge) fractions of .08,.12, and .15 respectively. Only a slight depression in T_c ($\sim$1.0 K) from that measured in a similarly prepared Nb_3Ge sample was observed. Unfortunately, no enchancement of the H_{c_2} was produced by the gallium additions; we measured dH_{c_2}/dT values of $\sim$2.23 + .02 T/K for two of these samples. This value is comparable with the average obtained in our CVD-prepared Nb_3Ge. This is surprising because ternary additons to Nb_3Sn and Nb_3Al have produced substantial enhancements of dH_{c_2}/dT. We plan to terminate work on gallium additions after one further attempt to prepare a sample with a gallium fraction exceeding 25%. A similar effort will be made to add boron to Nb_3Ge during the next quarter. This work is more fully discussed in Sec. III.

During this quarter we performed a microscopic inspection of several sections of tapes measured in our ac-loss studies. These examinations were aimed at discovering the origin of the high ac-losses measured in all of our samples with Nb_3Ge thickness $\geq$ 4.0 μm. These non-hysteretic losses are believed to be associated with currents flowing around the edge of the tape penetrating into the normal substrate. As discussed in PR-14, the large ohmic losses were not observed for tapes with Nb_3Ge thicknesses t $\leq$ 3.0 μm. We chose sections of tapes with t $\geq$ 4.0 μm and with t $\leq$ 3.0 μm and had their edges examined by scanning electron microscopy (SEM). We discovered that tape sections with t $\geq$ 4.0 μm had a continuous longitudinal crack running along one edge of the tape the entire length of the section. The tapes with t $\leq$ 3.0 μm showed no evidence of cracks. This investigation provides visual confirmation of the conclusions drawn in PR-14 from the ac-loss measurements. These results are presented in Sec. IV.

II. CABLE INSTRUMENTATION

In preparation for the actual attachment of the 1-m cable to BNL's superconducting transformer, additional instrumentation and minor modifications were implemented on the cable. In discussions with BNL personnel, it was learned that in previous BNL tests of 1-m and 10-m cables evidence was found for the presence of a radial component of the magnetic flux. While the origin of this radial component is not understood at present, it is believed that this flux contributes significantly to the measured loss, especially on the shorter 1-m cables. They have found that the radial flux is most prominent in regions near the ends of the cable. Such an observation suggests the radial flux may arise from a peculiar current path near the ends of the cable where the current transfers either from the outer co-ax to the inner or from the cable to the transformer. Even though the contribution from the radial flux to the total loss in the cable is not well understood, it was suggested by BNL personnel that we instrument our cable to measure this flux component.Its contribution to the loss could then be properly taken into account in the event that a better understanding of this effect is achieved at some latter date. To this end, we wound two sets of series opposition coils onto the outer surface of the outer co-ax, one set at mid-length along the cable and a second set situated about 15 cm from the shorted end of the cable. Each coil consisted of 40 turns of very fine copper wire. A center tap was provided on each coil pair so that the coils could be used to measure the axial flux as well as the radial flux.

In addition to this instrumentation BNL personnel suggested that we make some provision to enhance mechanical integrity of the cable to support the rather large radial forces arising from the interaction of the transport current and its self-field. This reinforcement was achieved by carefully wrapping 2-cm-wide teflon tape bands around the outer circumference of the cable. The bands were separated from each other along the length of the cable by about 2-cm.

Additional instrumentation that BNL will provide on the cable before it is placed in the test cryostat includes: 1) a Rogowskii loop placed concentric with the transformer lead to the inner co-ax from which the current measurement and compensation signal will be derived, 2) two thermometers attached to the outer surface of the cable to measure the helium gas stream temperature, and 3) a 600 turn pick-up coil located at the center-axis of the cable to measure the axial field.

BNL has available only one cryostat capable of variable temperature operation and 60 Hz current amplitudes $\geq$ 5000 A. Previous BNL programmatic commitments for this cryostat have delayed its availability for our use in testing the 1-m cable. At present, BNL's final 10-m cable is installed in this cryostat. Plans call for completion of testing on this cable by the end of April. We estimate that two weeks will be required to remove their 10-m cable, install our Nb_3Ge cable, and make the necessary pre-cooldown tests. Once this preliminary work is finished, we should be able to commence testing of our cable. Neglecting any unforseen delays, we expect to complete the ac loss measurements on our cable by the end of May.

III. TERNARY ADDITIONS TO Nb_3Ge

Nb-Ga Preparation

Using the chlorination technique described in PR-14, several runs were carried out in an effort to prepare stoichiometric Nb_3Ga. X-ray analysis of tape sections strongly suggested that as the Cl_2 flow through the Ga chlorinator was increased above 30 cm^3/min, a significant fraction of Cl_2 began to filter through unreacted. For this reason, attempts were directed at reducing the $NbCl_5$ flow while maintaining the chlorine flow through the gallium at 30 cm^3/min. At these very high H_2:Cl_2 ratios we were able to prepare Nb_3Ga containing only 22 at % Ga and could not achieve stoichiometry. Whether this is due to a problem with the gas mixtures chosen or is a result of selection of too high a deposition temperature is not understood at this point. Rather than continue the effort to deposit stoichiometric Nb_3Ga, we decided to use what we had learned about the thermodynamic properties of the Ga salts and attempt to prepare the ternary system Nb-Ge-Ga which was our original goal.

Nb-Ga-Ge Ternary Alloys

Previous work by Alterovitz et al.[3] on this system indicated only that gallium was extremely difficult to introduce into Nb_3Ge. Data presented graphically indicate that only about 1 at % Ge was successfully replaced by Ga. Other work by Bergner and Rao[4] seems to indicate that additions of Ga drastically lower the T_c of Nb_3Ge, reaching a low of 8 K at $Nb_3(Ge_{.25}Ga_{.75})$. Were this true, it would make the Nb-Ga-Ge ternary extremely interesting to study from the point of view of fundamental understanding. However, examination of the techniques employed suggest that these investigators have managed to prepare extremely non-stoichiometric alloys, and this, rather than a fundamental property of the ternary system, is what produces the low T_c's. In view of this, we felt that a study of the ternary system was well worthwhile, provided we were certain to use only deposits of known stoichiometry.

<u>X-ray Fluorescence Technique</u>

In a ternary system $Nb_x(Ga_{1-y}Ge_y)$ it is no longer possible to determine stoichiometry based solely on a measurement of lattice spacings. Empirically, we know that a given lattice spacing a_o, may result from many combinations of x and y, including many non-stoichiometric ($x \geq 3$) compositions. In addition, we are well aware, as a result of CVD experience in many other systems, that a given gas phase composition in no way implies the same composition in the deposit. This seems to be the trap that Bergner and Rao[4] fell into and must be avoided if the results are to be meaningful. The conclusion, then, is that we must have an analytical technique for unambiguously determining the composition of the alloy. The two most common techniques, wet chemical analysis and electron microprobe, are somewhat difficult to apply in this case. The small amount of material produced rules out wet chemistry as done at LASL. Microprobe requires careful calibration against known standards and, in addition, is extremely susceptable to sampling errors. By this we mean that electron penetration into the deposit is only of the order of a few hundred angstroms; hence only a surface layer is sampled. In CVD films, this is $\leq$ 1% of the total material and might represent an inconsequential surface layer deposited as the tape leaves the coating chamber, or even after it leaves the active deposition zone. For this reason, if microprobe sampling is to be carried out, the sample must be carefully ground and repressed so that the new surface represents a true cross section of the entire thickness. Achieving this can be very difficult with deposits only a few microns thick.

Fortunately, x-ray fluorescence techniques developed in Group M-1 at LASL can be of great help in this case. A sample of the material is exposed to 20 KeV x-rays from a radioactive cadmium source, and the resulting fluorescence is examined using energy dispersive techniques. Ordinarily this type of analysis also requires a number of calibration samples to account for inter-atomic absorption effects within the alloy. However, Ga and Ge, as a result of being adjacent in the periodic table, represent a special case. Shown in Table I are the values for the K_α and K_β x-rays as well as the K-absorption edge.

TABLE I

X-RAY DATA FOR GALLIUM AND GERMANIUM

	Ka Edge (keV)	$K_{\alpha 1}$ (keV)	$K_{\alpha 2}$ (keV)	K_β (keV)
Ga	10.37	9.25	9.22	10.26
Ge	11.10	9.87	9.85	10.98

It is clear from Table I, that the strong x-rays fluorescing from Ge($K_{\alpha 1}$) are too low in energy to excite the K-edge of Ga. This means that the inter-atom absorption effects between Ga and Ge will be very small. In addition, since they are adjacent in the periodic table, they will look essentially identical to the K_α x-ray of an element quite different in atomic number (i.e., Nb). The result of this analysis is that the observed ratio of Ga-K_α to Ge-K_α is very close to the actual atomic ratio of Ga to Ge and, for our purposes, may be used without correction. In addition to obtaining this ratio, we can also apply a correction to the observed Nb-K_α/(Ga-K_α + Ge-K_α) ratio to obtain an approximate Nb/(Ga+Ge) atomic ratio in the alloy. This correction is based on the observed Nb-K_α/Ge-K_α ratio in a Nb_3Ge binary alloy of known stoichiometry, and is used with the assumption that Ga and Ge atoms react in the same manner to a Nb-K_α x-ray.

Sample Preparation

A large number of runs have been carried out under a variety of flow conditions and at temperatures from 800° C to 940°C, with the bulk of the material prepared at 885° C. In general, Ga/Ge ratios determined by analysis were much lower than anticipated, and indicated that Ga activity in the gas phase is extremely low. Fig. 1 shows the relationship between Ga/Ge ratio in the deposit, and Ga/Ge ratio in the gas mixture. This extremely low Ga activity has caused considerable difficulty in preparing ternary alloys with large amounts of Ga. In addition to the difficulty in causing Ga to deposit, additional problems have been encountered with achieving stoichiometric Nb/(Ga+Ge) ratios. This determination is based in part on the use of the corrected Nb/(Ga+Ge) ratios obtained from x-ray fluorescence measurements. The measured ratio is considered along with the amount of second phase material present, and a composition for the A-15 phase is estimated. A somewhat more reliable determination is based on the measured Ga/Ge ratio and the predicted lattice spacing for that ratio using Vegard's law and the accepted values for Nb_3Ge (5.140 A) and Nb_3Ga (5.166 A). If the lattice spacing is close to the predicted value, the samples are assumed to be stoichiometric, while if it is significantly above the predicted value they are deficient in (Ga+Ge). The data for the 9 samples subjected to x-ray fluorescence are shown in Table II. As can be seen, of the total samples produced (40-50), only 3 were considered stoichiometric. This is a very low percentage and attests to the difficulty encountered in preparing this ternary system. The transition temperatures and lattice parameters of these three samples, along with the known endpoints (Nb_3Ge and Nb_3Ga) are shown in Figs. 2 and 3. Although less than 20% of the pseudobinary was established,

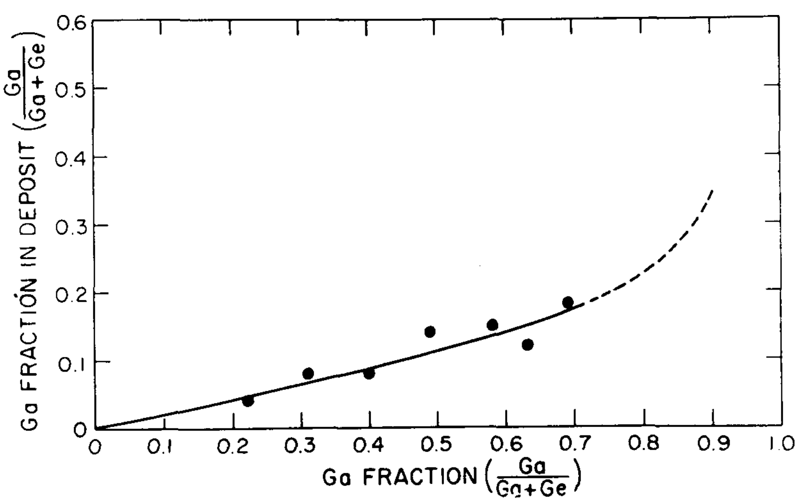

Fig. 1 A plot of the gallium fraction Ga/(Ga + Ge) in the deposit versus the same ratio in the gas stream.

Table II

X-RAY FLUORESCENCE DATA

Sample	Ga Fraction Measured	a_o (A) Predicted	Measured	A15(Ge+Ga)(at%) Calculated	dH_{c_2}/dT T/K	T_c (K)
DV945-3	0	-	5.140	+24.5		21.4
DV946-1	.04	5.1410	5.1422	21.6		19.9
DV946-2	.08	5.1420	5.1407	*23.7	2.5	20.5
DV947-3	.08	5.1420	5.1468	22.9		19.9
DV948-1	.14	5.1436	5.1516	23.2		16.9
DV950-3	.15	5.1438	5.1432	*26.1	2.2	20.5
DV952-2	.18	5.1446	5.1507	22.2		18.1
DV954-2	.12	5.1430	5.1447	*24.3		20.1
DV961-2	.22	5.1456	5.1497	22.2		--

*These samples are assumed to be stoichiometric based on a comparison of the predicted and measured lattice spacings, with additional consideration given to the calculated composition.

+ This binary sample was used as the basis for correcting the observed $(Nb\text{-}K_\alpha/(GeK_\alpha + GaK_\alpha)$ ratios.

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two important features are clear. First, the addition of Ga to Nb_3Ge results in a decrease in T_c. Second, this decrease is very shallow, indicating the remainder of the curve will probably show a minimum between 18 and 20 K. This, combined with measurements of H_{c2} on two of the stoichiometric samples
also showing a slight decrease, tends to predict that nothing exciting in terms of T_c or H_{c2} should be expected in the remainder of the pseudobinary. In view of this, the work on Nb-Ge-Ga will be terminated shortly so that Nb-Ge-B and Nb-Ge-Al can be investigated.

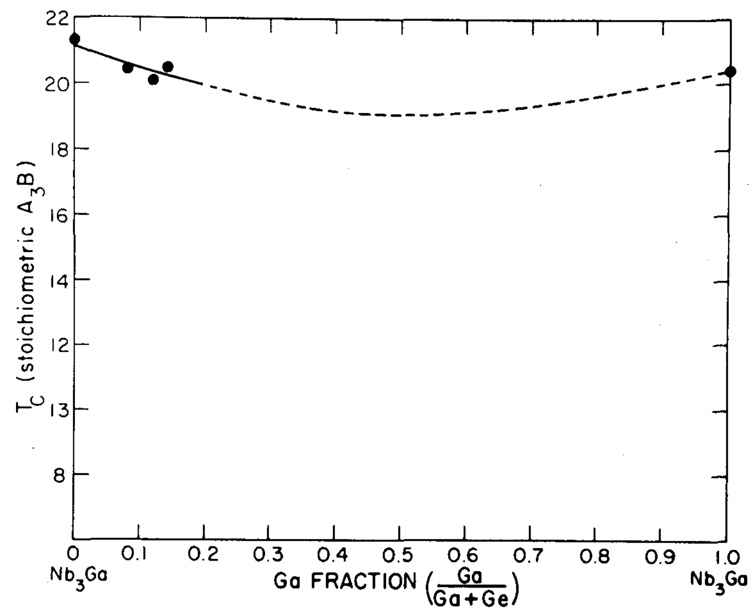

Fig. 2 A plot of the transition temperature T_c versus gallium fraction in the deposit for samples determined to be nearly stoichiometric.

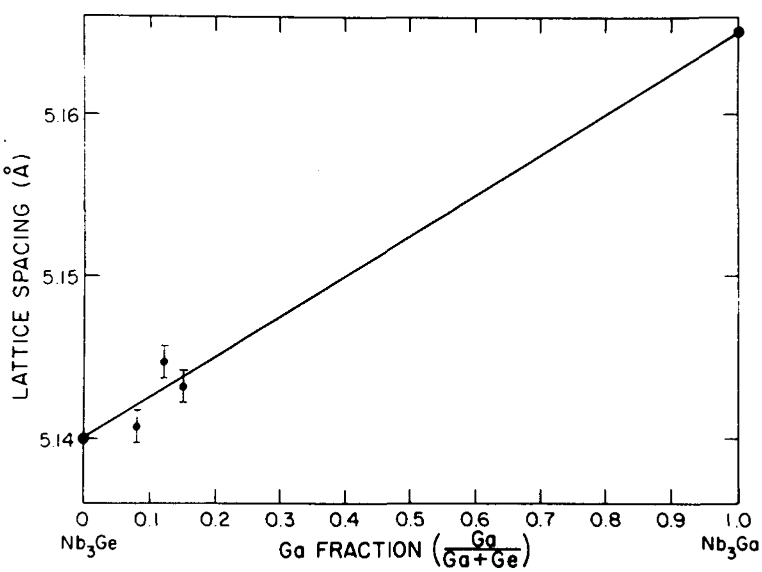

Fig. 3 A plot of lattice spacing versus gallium fraction for samples determined to be nearly stoichiometric.

IV. AC-LOSSES

As reported in PR-14, our ac-loss measurements revealed some interesting correlations for tape samples:

1. Without exception, all Nb_3Ge material with thicknesses ≥ 4.0 μm deposited on copper substrates exhibit large losses with a substantial ohmic component, indicating cracked edges.

2 Without exception, all Nb_3Ge materials will thicknesses ≤ 3.0 μm exhibit low losses with insignificant ohmic component, indicating edge integrity.

During this quarter, we conducted a microscopic examination of two of our tape samples, one an example of tapes with thick ($t > 4.0$ μm) Nb_3Ge coatings, and one with a thin ($t \leq 3.0$ μm) coating. Fig. 4 is a SEM micrograph showing an edge-on view of a section of sample DV 901 ($t \geq 5.0$ μm). Clearly evident is a longitudinal crack extending the length of the section. A scan of the 4.0-cm length shows that this crack is continuous throughout. Fig. 5 is an optical metallograph of the cross-section of this same tape segment, showing the crack extending from a sharp corner on the copper substrate (light area) to the surface of the Nb_3Ge coat. This is in contrast to a cross-sectional view, Fig. 6, of sample DV 913, where there is no evidence of any cracks. An examination by SEM of both edges of this sample, also showed no edge cracks. These findings corroborate our conclusions concerning edge cracks obtained from ac-loss measurements.

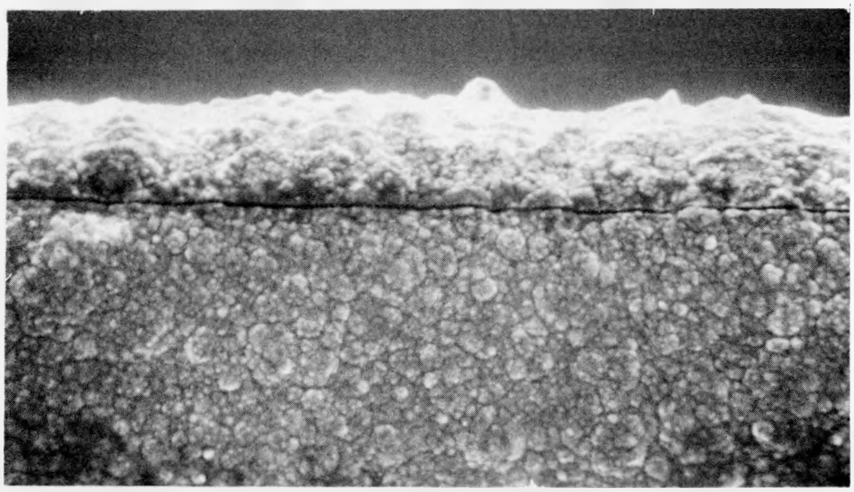

Fig. 4 SEM micrograph of an edge-view of a section of sample DV 901 showing a longitudinal crack extending the length of the section.

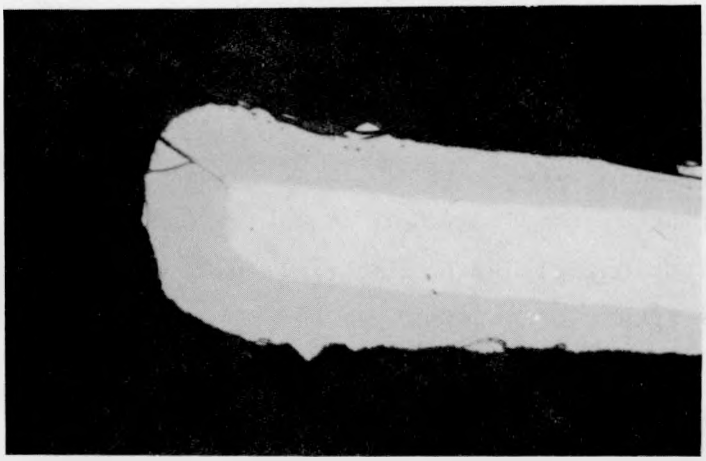

Fig. 5 Optical metallograph of a cross-section of sample DV 901 showing the crack extending from the upper corner of the copper substrate (light area) to the surface of the Nb_3Ge coat (darker area).

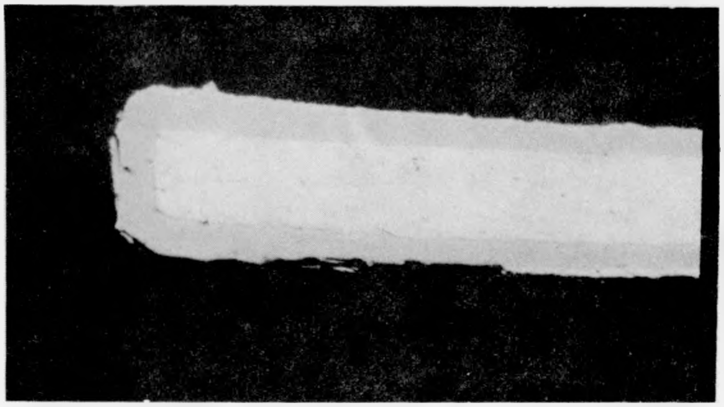

Fig. 6 Optical metallograph of a cross-section of sample DV 913.

Because the thinly-coated tapes (t $\leq$3.0 μm) carry sufficient current for transmission line applications, we now plan to fabricate conductors with t $\sim$3.0 μm for our second test cable. The fact that the crack on DV 901 appears to originate from a sharp corner of the substrate suggests that beveling the edges of the substrate after slitting may aleviate this problem. An investigation of tapes coated with thicker layers on substrates with beveled edges is planned for the next quarter. We have also commenced a theoretical thermo-mechanical analysis of the stresses encountered by our tapes during cool-down from the coating temperature. This analysis is aimed at understanding the relation between thickness and edge cracking in a qualitative manner. The two layers of the inner conductor of our first 1-m test cable were wound with tapes coated with 4-6 μm of Nb_3Ge and are expected to contain longitudinal cracks. The two layers of the outer conductor of this coaxial cable were fabricated from tapes coated with $\sim$ 3.0 μm of Nb_3Ge and should exhibit lower ac losses.

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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