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LASL Nb_3Ge Conductor Development

April 1—June 30, 1977

Compiled by

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LASL Nb_3Ge CONDUCTOR DEVELOPMENT

April 1 - June 30, 1977

Seventh Quarterly Progress Report

Compiled by

M. P. Maley

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ABSTRACT

The seventh 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 April 1 - June 30, 1977. Nb_3Ge coats, 4-6 μm in thickness, have been deposited by chemical vapor deposition onto long (1.0-m length) tapes which are pulled through the coating chamber. The substrate tapes are Ni and Cu, 0.64 cm wide and 25 μm thick. Critical currents in excess of 1200 A have been carried in two of these tapes with critical current densities reaching 2.4×10^6 A/cm^2 at 13.8 K. Problems involved with substrate compatibility and material uniformity are discussed. A transmission electron microscope (TEM) study of the microstructure of the material has been completed. The TEM micrographs show a fine dispersion of Nb_5Ge_3 precipitates throughout the material. A discussion of the relation of the microstructure to the enhancement of J_c by Nb_5Ge_3 is presented. A successful attempt at growing Nb_3Ge by epitaxy onto Ge-deficient Nb-Ge is reported.

I. INTRODUCTION

The Los Alamos Scientific Laboratory (LASL) program for the development of Nb_3Ge superconducting material has been sponsored by the Electric Power Research Institute (EPRI) since July 1, 1975. A review of the accomplishments of the program through July 1, 1976 may be found in the EPRI Final Report (TD-200) entitled "Development of Nb_3Ge Conductors for Power Transmission Applications."[1] The progress reports covering the period July 1, 1976 through March 31, 1977 have been issued by LASL as Reports LA-6607-PR, LA-6686-PR and LA-6798-PR, hereafter referred to as PR-D, PR-E and PR-F, respectively.

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This progress report covers the period April 1 - June 30, 1977 and is the seventh quarterly report since the beginning of the EPRI sponsorship. As was discussed in PR-F, the main emphasis of the program is directed presently toward the goal of reproducing on long continuous lengths of tape the superior superconducting properties which we have achieved on short samples. Considerable success has been achieved during this quarter in coating Nb_3Ge onto moving tapes of Ni and Cu. The substrate tapes are 0.64 cm in width and 25 µm thick and are coated with 4-6 µm of Nb_3Ge. Seven of the tapes coated carried currents of 800-1300 A at 13.8 K, implying critical current densities, J_c's, of 0.6 - 2.4 x 10^6 A/cm^2 at this temperature. The measured values of T_c*, the temperature at which the J_c versus T curve extrapolates to zero, ranged from 16.0 - 18.2 K. While our best tapes are approaching the performance achieved in short samples, several problems remain. Uniformity of material produced during a given run, reproducibility of results for a given set of process parameters, and selection of an optimum substrate are still unsolved problems. At the end of this reporting period, we discovered a contamination problem with the chlorinators which may have contributed to the lack of reproducibility and uniformity. The uniformity of the thickness across the width of the tape has been greatly improved by redesigning the mask structure to conform to the geometry of the tape. Our coatings appear to be continuous and regular around the edges of the tape.

A parallel effort toward optimizing Nb_3Ge in the short sample apparatus has continued. We have succeeded in growing three Nb_3Ge coats epitaxially onto Ge-deficient layers. This was accomplished by a continuous and gradual variation of the Ge-delivery rate. The three samples were all deposited at 800°C and exhibited identical values of 17.8 K for T_c*. This constitutes a considerable improvement in the value and reproducibility of T_c* for material deposited at 800°C. This result points to the importance of start-up conditions for the growth of the Nb_3Ge layer.

A study of the microstructure of our Nb_3Ge material by transmission electron microscopy (TEM) has been completed by T. E. Mitchell of Case Western Reserve University. The study shows that, for moderate concentrations (0-15 wt %) of Nb_5Ge_3, the σ-phase is dispersed as 100-1000 Å particles throughout the Nb_3Ge. The Nb_3Ge precipitates appear equally often at grain boundaries and within the A-15 grains. It would appear that they act both as primary pinning centers and as inhibitors to grain growth. A summary of the report by T. E. Mitchell is contained in Sec. V.

II. LONG-SAMPLE DEVELOPMENT

II-1 Substrate Materials

Nb and Ta were selected initially as substrate materials for the moving-tape coating apparatus because of their strength and of the close match of their coefficients of thermal expansion (CTE) to that of the Nb_3Ge coat. As was discussed in PR-F, severe cracking of the Nb_3Ge coats was encountered on a majority of the Nb and Ta tapes which were coated. The cause of this problem was discovered to be the hydriding of the substrate material, which takes place primarily when H_2 gas diffuses up the large space between the tape and the shielding tube wall. A change in the geometry of the shielding tube to a narrow slit was made in order to correct a coat-thickness variation problem, discussed below in Sec. II-2. It was hoped that the much smaller space in the slit geometry would also inhibit the upward diffusion of the H_2 against the slow Ar flow. It was clear that the slit geometry was very effective in preventing the coating gases from diffusing up the shield. However, one test run demonstrated that this solution was not effective for H_2. The tape tested was extremely brittle, but the brittleness did not extend onto the section remaining in the coating chamber at shutdown. This indicates that the bulk of the hydriding is still occurring in the upper shielding tube. It is now clear that the successful use of Nb or Ta as a substrate in the moving-tape apparatus will require a protective coating to shield the substrate from H_2 gases. A recent private communication from A. I. Braginski at Westinghouse indicates that a layer of Cu a few microns in thickness is sufficient to prevent hydriding. We plan to investigate this possibility during the next quarter.

Due to the fact that we have not yet solved the hydriding problem with Nb and Ta substrates, we have deposited the majority of the Nb_3Ge coats during this quarter onto Ni and Cu tapes. While neither of these materials is considered to be suitable as a final choice for the substrate, we have had considerable success with coating Nb_3Ge on them. We reported in PR-F that a Nb_3Ge-coated Ni tape carried 825 A of current at 13.8 K, implying a critical current density of 1.8×10^6 A/cm^2. This figure is approaching the best values which we had achieved on the short samples. During the present reporting period, seven Nb_3Ge-coated Ni and Cu tapes have been prepared which carried currents between 800 and 1300 A. These results, presented below in more detail in Sec. II-4, are encouraging. However, reproducibility of results, sample uniformity, and consistently high values of T_c* have not yet been obtained.

One problem observed, by metallographic examination, on samples coated on Ni tapes was the presence of a well-defined diffusion layer between the Ni and the Nb_3Ge coat. For tapes pulled at a rate of 1.0 m/h, this layer is approximately 2 μm thick and appears to grow from the deposit-substrate interface into the Ni substrate. More precise measurements will be made soon in order to confirm the direction of growth. The composition of the layer has been tentatively identified from x-ray diffraction work as Ni_3Nb. In itself this compound is not harmful to the tape, and, in fact, probably improves the bond between the deposit and substrate. However, the Nb which forms it must diffuse out of the deposit, and the effect of this on the properties of the Nb_3Ge is, as yet, unknown. If an alternative substrate to Ni is not introduced soon, this problem will have to be examined more closely.

Depositions were also made during this quarter on Cu-clad stainless steel and steel tapes. The object of this experiment was to further examine the adverse relationship which we have observed between the T_c* of the Nb_3Ge and compressive strain caused by differential thermal contraction between it and the substrate. The Cu-clad stainless steel tape was obtained from A. I. Braginski at Westinghouse. It offered the possibility of observing effects caused solely by strain without complications arising from diffusion between the substrate and the coat. Three tapes, Cu, Cu-clad SS, and steel were spot-welded together and pulled through the coating chamber under presumably identical deposition conditions. All three samples showed degraded critical currents. Problems connected with the chlorinator, discussed below in Sec. II-4, invalidated the results of this experiment. It will be repeated during the next quarter.

II-2 Nb_3Ge Thickness Variations and Edge Coating

Metallographic examination of the first tapes coated indicated a very large change in deposit thickness between the center and edge of the tape, as shown in Fig. 1a. This undesirable shape is largely due to the effects of shielding geometry on diffusion in the gas flow. As has been pointed out,[1] the gas flow in this system is quite laminar (Reynolds numbers <<100) and any protrusion into the flow stream casts a long shadow. It has been observed that, in the case of statically coated tubes, the 1.5-mm diameter supporting pins cast a noticeable shadow for ∿ 10 cm. In the case of a moving tape, the upper shielding tube, which prevents the coating gases from reaching the tape before the desired coating region, also casts a long shadow. The effect of this shadow may be regarded as being similar to a thick boundary layer, where coating gases from the moving stream are

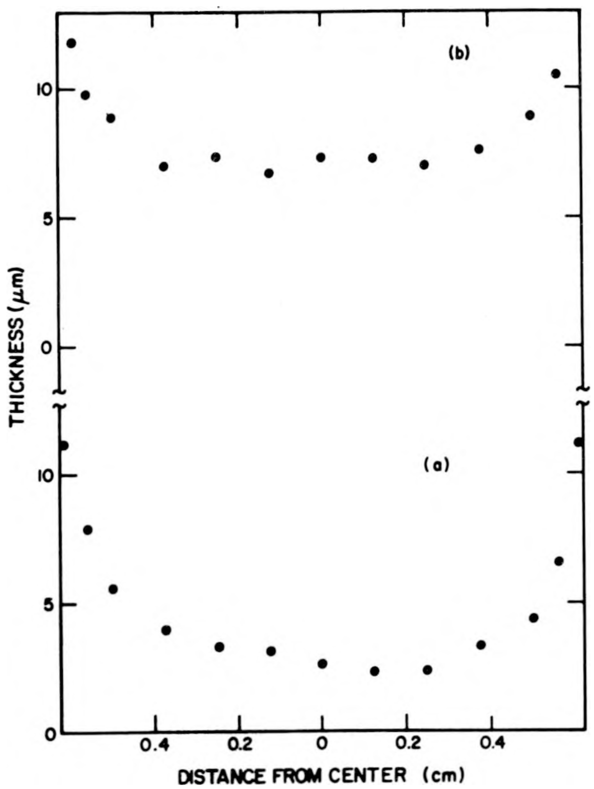


Fig. 1.
Plot of the thickness of Nb_3Ge coating along the width of a tape with a) a circular shielding tube and b) a slit shielding tube.

required to diffuse through a stagnant region in order to reach the substrate. The longer this characteristic diffusion path, the lower the coating rate at the substrate. In addition, it is possible that the properties as well as the deposition rate are affected.

The tapes with thickness variations like that shown in Fig. 1a were shielded by a circular tube $\sim$ 7.9 mm in diameter. This means that the center of a 6.4-mm wide tape is $\sim$ 3.9 mm from the gas stream while the edge is only 0.7 mm away, implying a much larger coating rate at the edge. Scaling the coating rate inversely as the minimum distance from the substrate to the gas stream is not quite correct, because diffusion can occur from many directions. A more accurate model would include an integral over these directions as in Eq. (1):

$$\left(\frac{1}{r(x)}\right)_{ave} = \int_0^{\pi} \frac{d\theta}{r(x,\theta)} . \qquad (1)$$

However, even using the simple approach (not integrated over θ), it is clear that a shielding tube shape similar to that of the tape would be desirable. Such a rectangular-shaped tube was formed, and the resulting thickness variation produced is shown in Fig. 1b. This represents a substantial improvement in uniformity and indicates that the ideas concerning diffusion paths have validity. Further efforts are underway to complete the flattening of this profile.

Another possibility which may be explored is the use of induced turbulence. It was noticed, quite accidentally, that the cross section of a piece of tape close (< 1.0 cm) to the follower rod was quite uniform, as shown in Fig. 2. It should be noted that the primary function of the follower rod in our system is to maintain tension, since we are not yet spooling the tape. It has a secondary

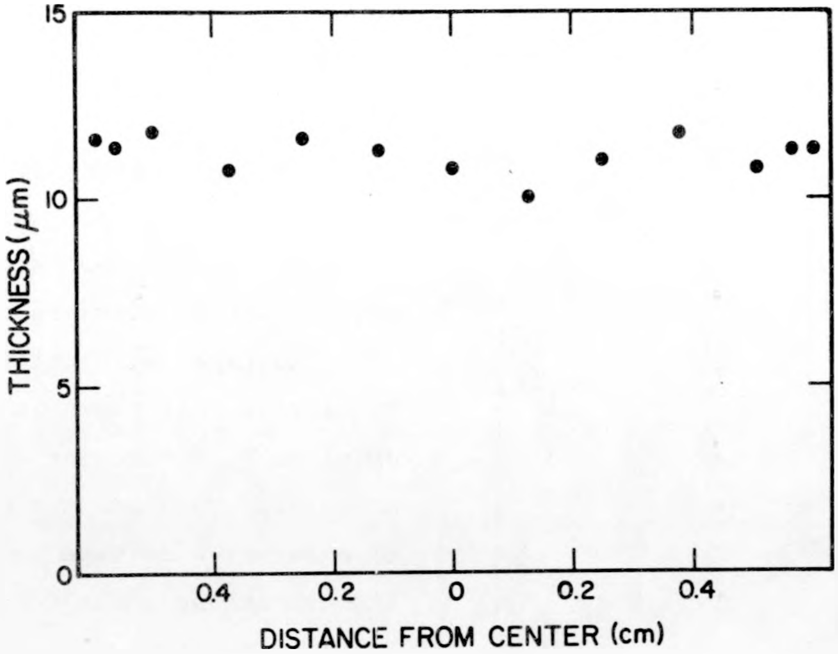


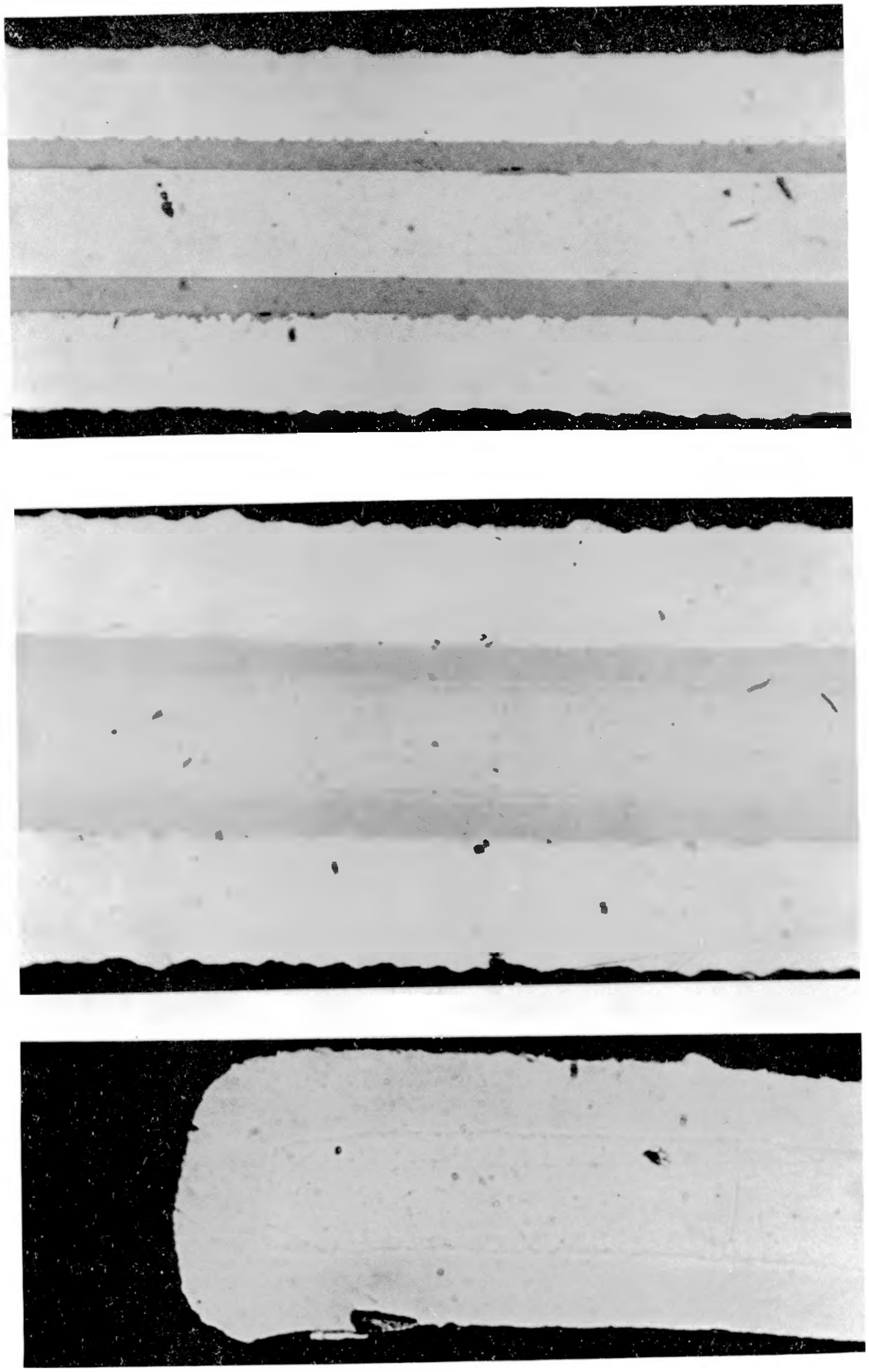
Fig. 2.
Plot of the thickness of Nb_3Ge coating along the width of a section of tape close (<1.0 cm) to the follower rod.

effect of causing turbulence in the gas flow where it attaches to the very bottom of the tape. This turbulence is responsible for the thickness profile shown in Fig. 2, and methods to deliberately induce such turbulence will be considered if the desired profile cannot be achieved by variations in shielding geometry alone.

A problem of some concern for superconducting tapes intended for application to ac power transmission is the growth of superconducting material around the edges. Shown in Fig. 3 are micrographs of two sections of tape which have been electroplated with Cu on top of the Nb_3Ge deposit. Figure 3a is a micrograph of a deposit on a 25-μm-thick Cu tape and Fig. 3b shows a similar deposit on a Ni tape. Close examination of the Ni tape reveals the diffusion layer, approximately 2 μm thick, which was discussed in Sec. II-1. Figure 3c shows a micrograph of a typical edge. Although the deposit is thicker at the edges due to considerations already discussed, there is no evidence of any strong dendritic growth or of any cracking.

II-3 Chlorinator Contamination

We experienced considerable difficulty during this quarter in correlating the superconducting properties measured with variations in the process parameters. In particular, as is discussed in Sec. II-4, the measured values of T_c* on Nb_3Ge-coated Ni and Cu tapes varied from 16-18.4 K. These values did not seem to cor-



a

b

c

Fig. 3.

Micrographs of cross sections of Nb_3Ge-coated tapes (magnification 600 X): a) Nb_3Ge-coated Cu tape; the two gray-colored strips are the Nb_3Ge layers b) Nb_3Ge-coated Ni tape; the two parallel gray strips are the Nb_3Ge with the diffusion layer appearing at their inner borders c) Edge of a Nb_3Ge-coated Ni tape.

relate with any of the parameters controlled or measured, such as deposition temperature and Nb_5Ge_3 content. The variation does, however, show a very rough correlation with the length of time that a particular chlorinator has been running. This variation is shown in Fig. 4 for the two most recent chlorinators. The most probable explanation for this behavior is contamination by impurities in the chlorine supply. The filtering chamber, filled with "Dryrite," has been in use for $\sim$ 500 coating runs and may be exhausted. Several runs were made using a new chlorinator and with the filtering chamber removed and several more with a new filtering chamber added. It is expected that the determination of the T_c*'s of the material produced in these runs will allow a better understanding of the effects of contamination.

II-4 Superconducting Properties

II-4.1 Analysis Problems

The shift from tube to moving tape geometry and the use of Ni as a substrate has caused substantial difficulty in carrying out x-ray analysis and has diminished the amount of useful information obtained by other techniques. The most significant problem is the failure to obtain any powder samples from the tapes. It has not been possible to remove the deposit from the 25-μm-thick Ni substrate mechanically, and no etchant is available which will attack only the Ni and not affect the Nb_3Ge deposit. This lack of powder samples prohibits accurate

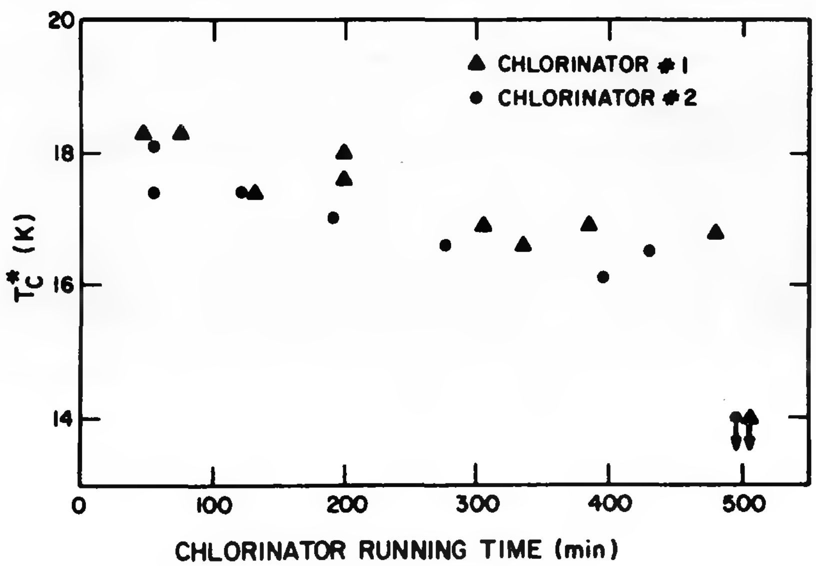


Fig. 4.
Variation of measured values of T_c* for Nb_3Ge material versus accumulated chlorinator running time.

measurement of Nb_5Ge_3 content as well as Debye-Scherrer patterns for accurate lattice spacings. Some information can be obtained from diffraction patterns of tape sections mounted on glass slides. However, lattice parameters can be noticeably affected by substrate compression, and the accuracy of Nb_5Ge_3 determination is severely limited by preferential grain orientation and contributions from Ni_3Nb diffraction peaks. As a result, much greater reliance must be placed on measurements of critical current density, J_c, and on ac-loss measurements than in the past. This results in a longer time delay in determining the effects of process parameter changes, since these are necessarily more time-consuming measurements than the x-ray work used previously.

The four-probe dc transport measurements, which provide the principal information on the superconducting properties of the tapes at present, also encounter problems associated with the use of Ni substrates. As shown in Table I, a good tape may carry 500-1300 A at 13.8 K, depending upon its cross section. When I_c is exceeded and some portion of the tape is driven normal, considerable heating can take place before the current supply is turned off, as there is no high-conductivity path for the fault current to take. Figure 5 shows I_c versus T plots for three different Nb_3Ge-coated Ni tapes. Figure 5a shows the data for a tape which apparently suffered no damage. Figure 5b shows a similar curve for a tape which burned in half during the measurement. On removal from the liquid hydrogen bath, this tape had clearly melted edges, indicating that the melting point of Ni was exceeded. Figure 5c shows a result frequently observed, where the tape is apparently damaged each time the current is ramped up, but not burned in half. If a tape like this is repeatedly driven normal at the same temperature, I_c will become successively lower. The I-V curves of all of these Ni-substrate tapes exhibit a sharp jump to the normal state rather than the "rounded knee" observed for Nb_3Ge deposited on a Cu substrate.

Two measures have been employed to combat this problem, with partial success. First, 25 μm of Cu is electroplated over the entire length of the sample to be measured. Good adherence of the Cu to the Nb_3Ge is required, both for protection of the coat when I_c is exceeded and also in order to avoid heating at the current contacts. This latter problem was discussed in PR-F. It was discovered that good adherence of the Cu electroplate could be obtained if the Nb_3Ge surface was lightly etched prior to plating and if the bath conditions were maintained carefully at 30 mA/cm^2 current density. It was found that under these conditions good electrical contact could be achieved between the Cu and the Nb_3Ge, as evi-

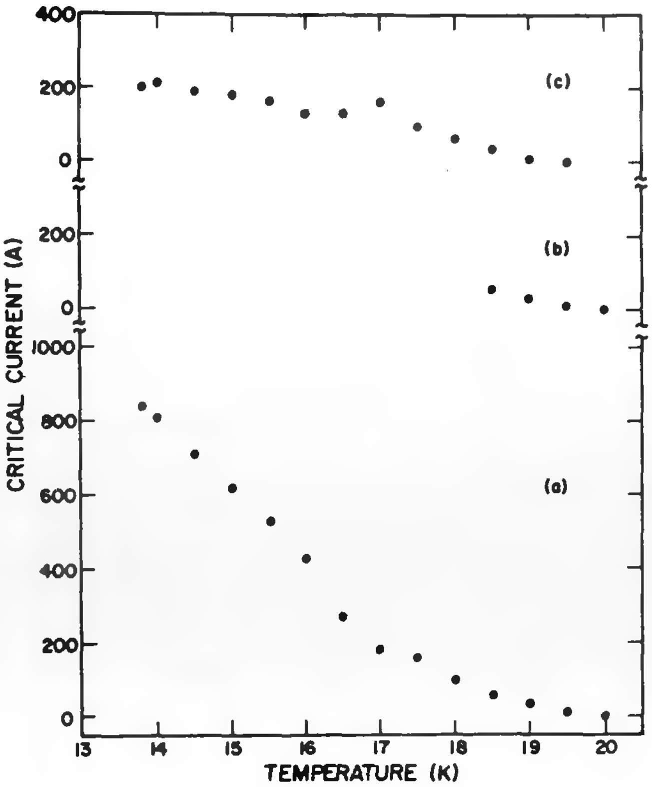


Fig. 5.
Critical current measured by four-probe resistance measurement versus temperature for a) undamaged tape; b) tape which burned through c) damaged tape.

denced by the absence of detectable contact resistance at currents of 1000 A. The electroplate unfortunately contains considerable H_2 and, therefore, is quite tough, having much lower conductivity than pure Cu. For these reasons 25 μm of electroplate on each side cannot completely carry the large fault currents without excess heating. Thicker electroplated Cu deposits would probably put the Nb_3Ge under a large compressive strain because this Cu is "tough pitch" and will not yield well. Annealing attempts at 300-550°C, aimed at removing the H_2 and softening the Cu, were not successful since they resulted in separating the electroplate from the deposit. The second measure employed to correct this problem has been the introduction of a fast trip in the current supply. The trip is designed to shut off the power supply within 5 ms after the voltage sensed across the entire sample reaches 200 μV. This measure was successful in protecting the samples from damage. It appears that the long-range solution to this problem is either to deposit the Cu by sputtering, as is presently being done by Braginski at Westinghouse, or to electroplate a thin layer (< 10 μm) of Cu followed by a layer of high-conductivity Cu soldered on top.

II-4.2 Results of Critical Current Measurements

Table I is a summary of the results of the four-probe resistance measurements on samples produced during this quarter. A substantial number of the tapes carried currents $I_c \geqslant 800$ A, with critical current densities varying from 0.3×10^6 A/cm^2 - 2.4×10^6 A/cm^2 at 13.8 K. The Nb_3Ge material deposited on the better tapes is thus comparable with the best short-sample material which we had produced previously. As noted in the table, many of the tapes were damaged during the measurement, and the values of I_c listed are lower limits for the weakest links in the tapes. As discussed in Sec. II-4.1, the absence of stabilizing Cu caused thermal "runaway" for the whole tape once the critical current for any part of it was exceeded. The values of T_c* ranged from 16.0-18.2 K. Aside from the problem with the chlorinator discussed in Sec. II-3, it is felt that the variation of the properties of the tapes is primarily due to mechanical damage. Neither Cu nor Ni has sufficient strength in the fully annealed condition to be a suitable substrate. Greater attention will be given to solving the substrate problem during the next quarter.

III. STATIC EPITAXIALLY GROWN DEPOSITS

Concurrent with the long-tape development work, we are continuing efforts toward improving the superconducting properties of the Nb_3Ge on a separate short-sample coating apparatus. During this quarter we have begun studies on Nb_3Ge grown epitaxially upon Ge-deficient Nb_3Ge material. Work reported by Dayem et al.[2] on Nb_3Ge grown epitaxially on top of a layer of Nb_3Ir of varying lattice parameter indicates that epitaxy based on lattice parameter can occur in this system. We have tried a modification of this technique. Instead of starting from the desired lattice spacing using Nb_3Ir, we start from a Ge-deficient A-15 and slowly increase the Ge to the desired level. As a result, the lattice parameter should vary extremely slowly between atomic planes, and epitaxial growth should be possible. The static runs were made in this manner at 800°C with very encouraging results. All three runs had identical values of T_c* of 17.8 K even though the final Ge content varied. Examination of T_c* versus deposition temperature studies made previously, and discussed in PR-E, indicates that this value of T_c* is about 1.0 K higher than the average value observed for samples deposited at 800°C. Inductive transition curves run on these three samples were quite

TABLE I

SUMMARY OF CRITICAL CURRENT MEASUREMENTS ON Nb_3Sn-COATED TAPES

Sample #	Substrate Material	Critical Current @ 13.8 K,A	T_c*,K	Comments	Mean Thickness	J_c A/cm^2
DV 707	Steel	784	17.5	damaged	2.8 μm	
DV 709	Ni	842	18.2		2.8 μm	2.4×10^6
DV 710	Ni	500	17.3			
DV 711 A	Ni	200	-	damaged		
DV 711 B	Ni	220	-	damaged		
DV 717		400	17.0			
DV 712 A		225	17.25	Cu-plate, 10 μm		
DV 712 B	Ni	420	18.0			
DV 715		120	16.6			
DV 716 A	Ni	51	16	damaged		
DV 717 2		215	16.25	Cu-plate, 10 μm		
DV 720	Ni	350	16.75	damaged		
DV 723	Ni	270	16.35	damaged		
DV 724 A	Ni	130		damaged	4.0 μm	0.3×10^6
DV 724 B	Ni	300			4.0 μm	0.6×10^6
DV 724 C	Ni	900		Cu-plate, 50 μm	4.0 μm	1.8×10^6
DV 725	Ni	810	17.25	Cu-plate, 50 μm		
DV 727	Ni	1250	17	Cu-plate, annealed, 50 μm		
DV 730 A	Ni	235	15.6	Cu-plate, 25 μm		
DV 730 C	Cu	1330	16.6	Cu-plate, 25 μm		
DV 733	Ni	910	16.2			
DV 730 B	Cu-clad SS	1160	16.0			

sharp ($\Delta T_c \sim 1.0$ K) with the highest onset occurring at $\sim$ 21.6 K, again about 1.0 K higher than any inductive T_c's we have previously measured on material deposited at 800°C. The very encouraging feature of these tests is the reproducibility of T_c*. If this result is not accidental for these three samples, it could indicate that much of the previous variation in T_c* is due to the exact nature of the start-up conditions. In other words, the amount of Ge in the A-15 structure may depend not only on the parameters (e.g., composition) in the gas stream during cooling, but also on the detailed history of how they were brought to these values. We intend to pursue this study during the next quarter.

IV. AC LOSSES

During this quarter we have constructed and performed preliminary tests on a new apparatus for measuring ac losses in Nb_3Ge deposited onto tape substrates. The sample holder, similar in concept to that used at Westinghouse for loss measurements on superconducting tapes, is sketched in Fig. 6. It consists of a phenolic bobbin, 1.75 cm in diameter, onto which six equally spaced flats, each 0.64 cm wide by 1.9 cm long, have been machined. With this design several variations of sample configurations can be employed:

(1) 0.64-cm x 1.9-cm sections of Nb_3Ge tape can be placed on each of the flats;

(2) two 0.64-cm wide by 4.4-cm long tapes can be stacked side by side and wound around the circumference of the bobbin; or

(3) one 1.3-cm wide x 4.4-cm long tape can be wound around the bobbin circumference.

The ac losses are measured using the standard lock-in amplifier technique employed for loss measurements on the Nb_3Ge-coated tubes.[1] The hysteretic loss signal is detected by a 115-turn pickup coil, which first was wound onto a suitable length of 50-μm-thick mylar tape that later was flattened upon itself such that the sample tapes could be inserted inside the coil windings. Compensation of the undesired inductive signal in the pickup coil was accomplished by a 150-turn compensating coil wound on a former placed along the axis of the phenolic sample holder. (See Fig. 6.)

During the measurements, the sample holder is placed at the center of an ac solenoid with the axis of the bobbin aligned with the axis of the solenoid. As a result of the various possible sample configurations, measurements can be performed on 0.64-cm-wide tapes with the induced currents running either around their

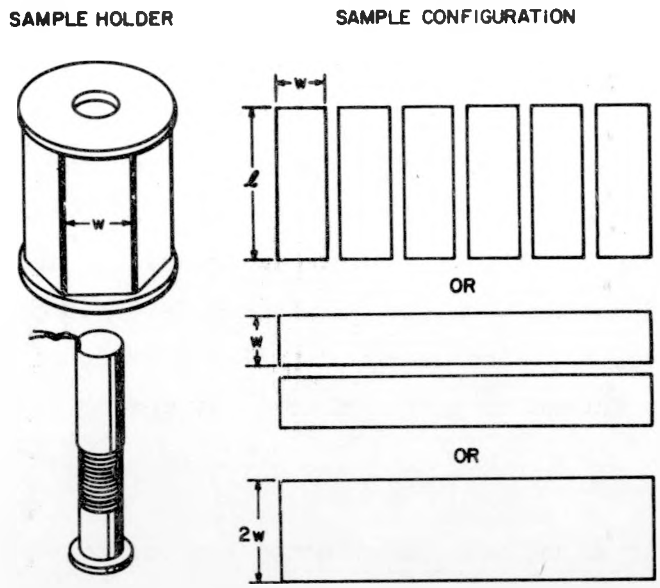


Fig. 6.
Shown at the left is a sketch of a sample holder and compensating coil insert for measuring ac losses in tape samples of Nb_3Ge. At the right, three possible sample configurations, all compatible with the holder, are shown. In all three cases the samples are situated in a pickup coil placed circumferentially about the diameter of the sample holder.

circumference or along the length of the tapes (comparable to the dc transport measurements) and on 1.3-cm-wide tapes with the induced current longitudinal. It is particularly important that when the current is induced circumferentially about the tapes that the Nb_3Ge coat be continuous around the tape edges in order to avoid a large nonhysteretic signal arising from the passage of the induced currents through the nonsuperconducting substrates. This problem is present also in the other sample configuration, but in this case,the signal arising from ac currents flowing through the substrate at the ends of the tape is a much smaller fraction of the desired hysteretic signal. One disadvantage of wrapping the tapes around the bobbin circumference is that the Nb_3Ge coat is placed under strain. For the present arrangement, a coat 4 μm thick is strained slightly less than 0.2%. This may be sufficient to cause some degradation in the superconducting properties. At present the bobbin diameter is limited by the ac solenoid bore, but this problem will be remedied by replacing the present solenoid by one with a larger bore.

Preliminary measurements have been performed on both Nb and Nb_3Ge tapes. Initial testing on 50-μm-thick Nb foil wrapped around the bobbin circumference indicated that the new apparatus worked acceptably well, with the hysteretic loss waveform, $\frac{d\phi}{dt}$ vs t, appearing identical with that observed on Nb tubes and rods. Measurements made on Nb_3Ge coated onto Ni-substrate tapes, however, exhibited anomalous hysteretic waveforms which were not compatible with critical state models. In addition, the presence of a nonhysteretic loss component indicated that the ac field was penetrating into the Ni. This may be caused by cracks introduced into the Nb_3Ge coat by subjecting it to a small bending radius. We will continue ac-loss measurements on tapes in a larger bore magnet during the next quarter.

V. MICROSTRUCTURE STUDIES BY TEM

V-1 Introduction

During the period Oct. 1 - Dec. 31, 1976 we began a study of the microstructure of Nb_3Ge material by transmission electron microscopy in collaboration with T. E. Mitchell of Case Western Reserve University. Ten samples of Nb_3Ge were deposited onto the inside surfaces of Cu pipe at various deposition temperatures and containing varying concentrations of Nb_5Ge_3. The motivation for this study arose from the observation of a strong correlation between J_c and the concentration of the σ-phase Nb_5Ge_3 for samples deposited at the same temperature, T_D.[1,3,4] The precise form of this correlation was a strong function of the deposition temperature, but, typically, for $T_D \geqslant 800°C$, there is a peak in J_c at concentrations of $Nb_5Ge_3 \sim 3-7$ wt %. It thus appears that a few per cent of Nb_5Ge_3 acts to increase the density of pinning centers and to enhance J_c substantially. In addition, we observed a strong tendency for J_c to increase with decreasing deposition temperatures. For purposes of optimizing Nb_3Ge material for high critical current densities it is important to understand the microstructural features which provide strong pinning. In particular, it is important to know the function of the Nb_5Ge_3 in enhancing pinning. If the Nb_5Ge_3 agglomerates at grain boundaries it would limit grain growth, implying that grain boundaries are the primary pinning centers in the material. On the other hand, dispersion of the Nb_5Ge_3 as small particles within the A-15 grains would support the view that Nb_5Ge_3 precipitates are acting as primary pinning centers. It is of further interest to investigate how σ-phase particle size and dispersion is influenced by deposition temperature and concentration. All of these structural properties could be revealed by TEM.

V-2 Experimental Procedures

The samples were prepared at LASL and sent to T. E. Mitchell at Case Western Reserve University, where the TEM study was performed. The coatings of Nb_3Ge were generally 15-30 μm thick. The Cu tubing was dissolved away in dilute nitric acid. Specimens were picked up on 3-mm stainless steel grids and rinsed. Since the specimens were too thick for electron transmission, they were thinned by ion milling until a hole appeared (∿ 3 h). Specimens were examined either at 650 kV using a Hitachi HU-650 B high-voltage electron microscope or at 125 kV using a Siemens Elmiskop 102 high-resolution electron microscope. The foils were found to be transparent enough so that the high-resolution microscope was used most of the time. Ion thinning gave no perceptible radiation damage; however, surface contamination was occasionally observed, which could easily be distinguished as an artifact.

The following electron microscopy techniques were used:

(a) Selected area diffraction (SAD). In general, the grain sizes and precipitate sizes were $\leqslant 0.1$ μm, which is much less than the minimum useful SAD size (∿ 1 μm). Hence single crystal patterns were rarely obtained. Spotty ring patterns were normal, containing both A-15 and σ-phase reflections. Only the inner $[110]_\sigma$ spots could be distinguished with confidence and they were often invisible on the screen.

(b) Bright-field microscopy. This was found to be the best method of obtaining an overall view of the microstructure. With the help of some dark-field microscopy (below), it became simple to distinguish visually between the larger A-15 grains and the smaller σ particles.

(c) Dark-field (DF) microscopy. The best way to image the σ particles with confidence was found to be with the $[110]_\sigma$ reflection. However, having done this a a few times (and realizing the particles could only be imaged one at a time in this way), we found the BF technique to be satisfactory. The DF microscopy was also employed using the $[210]_{A-15}$-$[420]_\sigma$ ring; this was successful in highlighting single A-15 grains and σ particles which happened to be diffracting strongly.

(d) Phase contrast microscopy (lattice imaging). This was accomplished by using a large objective aperture, allowing the central beam to interfere with various diffracted beams by underfocusing. In principle, this is an excellent technique to distinguish between the phases and it was performed successfully; but because of the high magnifications (∿ 50,000 X), limited field, and extreme sophistication, the technique was abandoned for routine examinations.

V-3 Results

V-3.1 General Microstructural Features

Examination of the micrographs reveals the following features:

a) Grain boundaries (A-15 phase) - distinguishable as lines, boundaries between dark and light regions, thickness fringes, and occasionally as dislocation networks. Figure 7 is a micrograph of Sample V479, which shows the grain structure clearly. This sample was deposited at 835°C and contained $\leqslant$ 2.0 wt % of Nb_5Ge_3. This micrograph is representative of material deposited at T_D > 800°C and containing very little Nb_5Ge_3. It is characterized generally by a low value of J_c.

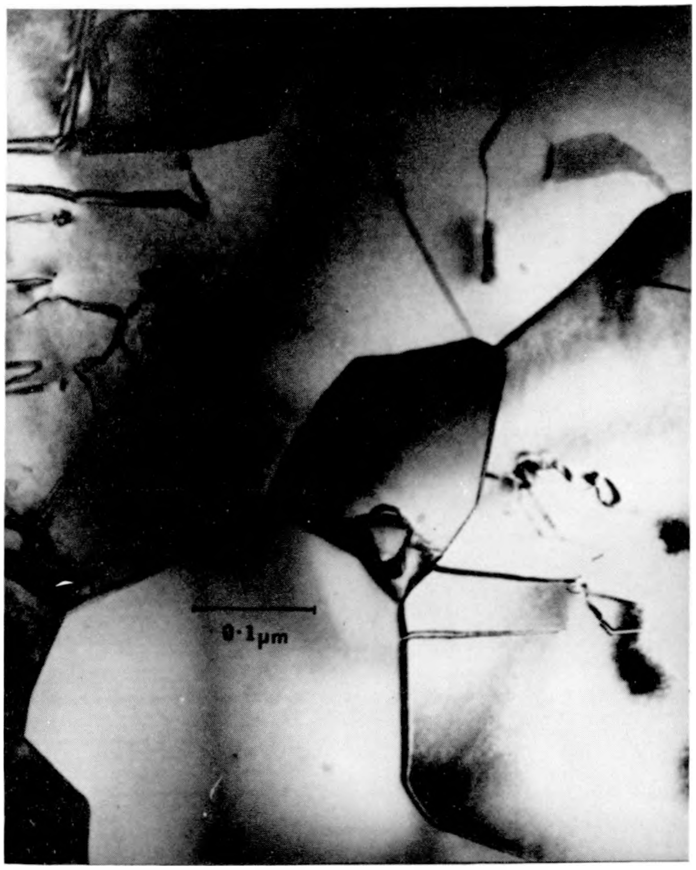


Fig. 7.
Transmission Electron Micrograph (TEM) of Sample V479. The grain structure apparent in this sample is typical for samples deposited at temperatures >800°C and containing small amounts of Nb_5Ge_3 precipitate. This microstructure is characteristic of low J_c material.

b) <u>Precipitates (σ-phase)</u> - distinguishable as smaller than the A-15 phase, usually darker but often lighter, sometimes round and sometimes angular, and (in the Ge-rich alloys) sometimes clustered. They may be inter- or intra-granular. Figure 8 shows the structure of Sample V490 with T_D - 835°C and with 5-7 wt % of Nb_5Ge_3. The σ-phase particles are clearly visible as the smaller particles equally dispersed throughout the material and at the grain boundaries. This type of microstructure was characteristic of samples with a high value of J_c.

c) <u>Precipitates (unknown)</u> - distinguishable as a "tweedy" structure, mostly but not always at grain boundaries, varying somewhat but present in all the samples.

d) <u>Dislocations</u> - these were surprisingly rare and varied little from sample to sample.

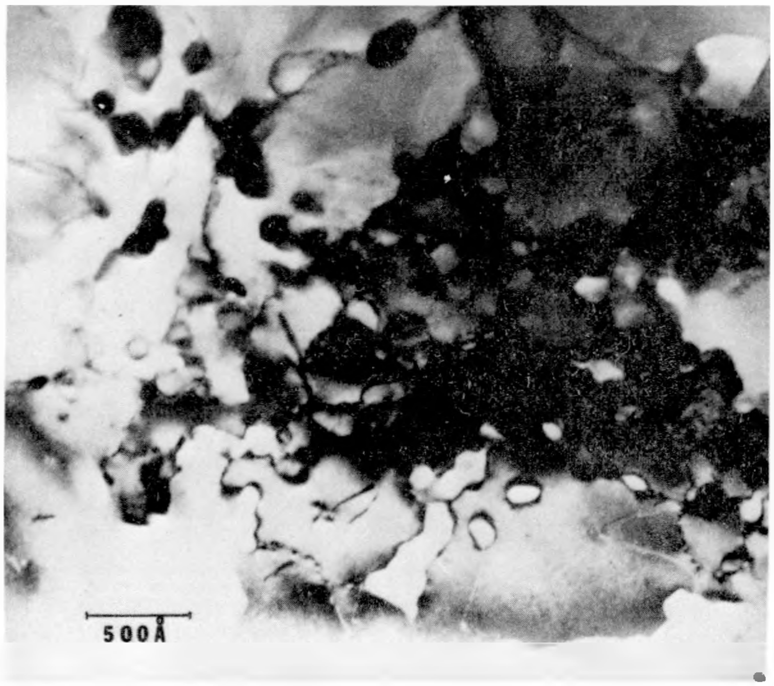


Fig. 8.
Transmission Electron Micrograph (TEM) of Sample V490. Nb_5Ge_3 particles are visible as smaller particles dispersed throughout the A-15 phase. This type of microstructure is characteristic of samples exhibiting high critical current densities.

e) Antiphase domain boundaries - distinguishable as a wavey line or as symmetrical fringes (parallel to the surface) in the A-15 structure. This is the dominant defect in Nb_3Ge but does not vary much from sample to sample.

f) Strain contrast - distinguishable as dark and light shadows in the A-15 phase around the precipitates. This feature is less apparent in samples with small amounts of σ-phase deposited at the higher temperatures. These features are described in more detail below.

As described later, the grain size tends to decrease with decreasing temperature and increasing σ content.

V-3.2 A-15 Grain Structure and Size

Grains are presumably columnar but there is no way of ascertaining this by TEM. Grain boundaries are mostly high angle with occasional low-angle boundaries (dislocation networks). The boundaries are reasonably straight and smooth. Grain sizes were measured from the average of $\sim$ 30 grains and are given below in Table II. The grain size varied considerably within a given alloy, especially for alloys rich in σ-phase.

V-3.3 σ - Nb_5Ge_3 Precipitates

(a) Coherency - in spite of the similarity in unit cell, the σ particles are oriented randomly with respect to the A-15 matrix, are thus incoherent and sometimes associated with interfacial dislocations. Moire fringes are often observed around precipitates, apparently due to an accidental orientation relationship. Matrix strain contrast around σ particles is observed in the higher alloys such as might be expected from misfitting spheres, but this must be due to differential thermal contraction rather than coherency strains.

(b) Morphology - σ precipitates appear in both a rounded form and an angular form, the latter often hexagonal. The only correlation appears to be with deposition temperature, which, if low, favors rounded particles.

(c) Distribution - there is a slight tendency for the σ precipitates to favor the grain boundaries, the tendency increasing with increasing deposition temperature. The distribution is generally uniform except in the Ge-rich alloys in which the precipitates tend to occur in clusters.

(d) Size - precipitates vary in size from 100 to 1000 Å. There is no correlation with alloy content but the larger precipitates tend to occur at the higher deposition temperatures.

(e) Internal structure - none is discernible in the way of defects.

V-3.4 Dislocations

A-15 grains appear to be quite "clean" with very few dislocations, especially at the higher deposition temperatures and lower second-phase alloys. The highest dislocation density is in Sample 563, which was deposited at 800°C.

V-3.5 Antiphase Domain Boundaries

Antiphase Domain Boundaries (APB's) in Nb_3Ge are very prominent in all the alloys. Whenever single crystal patterns have been obtained, trace analysis has shown that the APB's prefer [100] planes with a secondary preference for [110] planes. The APB density varies quite widely, even in the same alloy, but shows little systematic variation, possibly increasing with increasing Ge content. APB's frequently terminate at particles. The domain size is about 200-500 Å in diameter. APB's are most evident in the larger grains.

V-3.6 Other Precipitates

The most prominent secondary precipitate is a "tweedy" structure which occurs in all of the alloys except Sample 567 and generally, but not exclusively, prefers grain boundaries. The nature of the precipitate is unknown, but no serious effort has been made to identify it. Presumably it is an impurity phase, but possibly it is the T-2 phase referred to by Braginski et al.[5] Diffraction patterns showed prominent streaking perpendicular to the tweed pattern and also some very closely spaced spots (> 10 Å), indicating a large unit cell. The tweed structure itself appears to be due to structure factor contrast, rather than strain contrast, and may therefore be due to a very fine scale (< 100 Å) duplex-phase structure, such as might occur by spinodal decomposition. The tweed precipitate is displayed prominently in alloy Sample 443B but is present in the others to the extent of 1-5% with no apparent correlation with the material variables.

V-3.7 Effects of Deposition and Nb-Ge Composition

The main microstructural features are summarized below in Table II where the alloy samples are listed in order of increasing Nb_5Ge_3 content.

(a) Grain size. Grain size is plotted against % σ in Fig. 9. It is seen that there is a strong trend for grain size to decrease with increasing % σ and decreasing CVD temperature.

(b) σ Precipitates. The size of these precipitates, like the A-15 grain size, tends to decrease with decreasing CVD temperature and increasing Ge content, although there is considerable scatter. The precipitate distribution is quite uniform in the low alloy Samples 567, 443, 415 and 479, while some clustering is

TABLE II

SUMMARY OF GRAIN SIZE DETERMINATIONS

Alloy Sample	Temp.	% σ	Grain Size (μm)	σ Size (Å)	Tweed Size (Å)	Tweed %	APB Density
567	800	0.8	0.27	-100	-	-	Low
443B	900	1.7	0.60	<1000	∿500	∿5	Low
443C	900	1.7	1.3	∿1000	-	-	High
415	850	1.8	0.40	∿100	∿1000	∿5	High
563	800	1.5-2.7	0.20	∿100	∿1000	<1	Some high
479	835	3	0.47	∿200	∿200	<1	Some high
490	835	7	0.17	∿100	∿500	∿1	High
427	850	7-15.4	0.45	∿1000	∿1000	∿2	Medium
425	850	27	0.22	∿1000	≳1000	∿2	High
401	835	29	0.14	∿100	∿1000	<1	High
568	750		0.46				

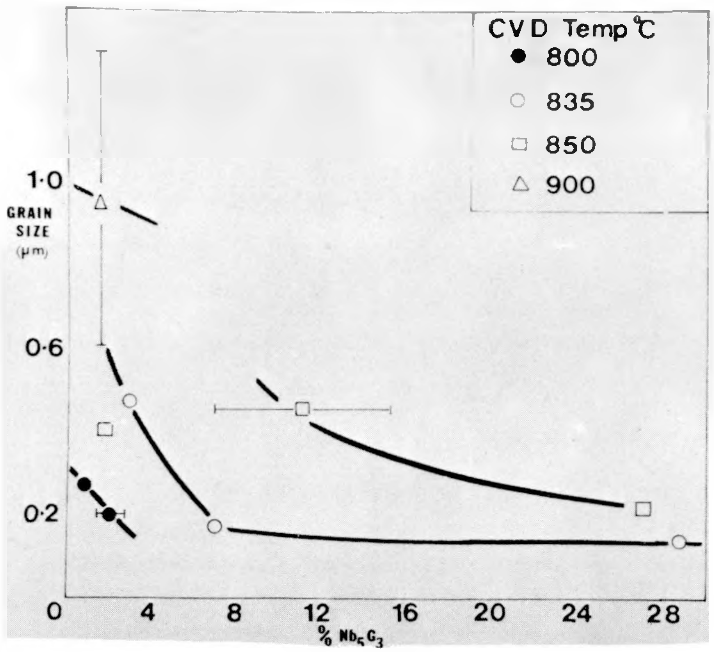


Fig. 9.

Plot of the average Nb_3Ge grain size as a function of weight % Nb_5Ge_3 content in the A-15 matrix. Note a strong trend for grain size to decrease with increasing Nb_5Ge_3 concentration and decreasing CVD temperature.

apparent in the medium alloy Samples 490 and 427. In the high alloy Samples 425 and 491 the precipitates are mostly clustered. The low alloy Sample 563 is a bit anomalous in showing some clustering.

(c) Tweed Precipitates. As shown in Table II, the tweed precipitate size tends to increase with increasing Ge content (in contrast to the σ size). The % tweed is unsystematic except possibly for a tendency towards higher concentrations at higher CVD temperatures.

(d) APB's. The APB density is high in all cases except for Sample 567. Typically there are 10 or more domains in each A-15 grain, especially in large grains. APB's may be important in pinning flux lines; however, there are no systematic changes which could be correlated with critical current density as a function of alloy content or CVD temperature. APB's frequently terminate at partial dislocations but, in general, the dislocation density is insignificant.

The most important changes appear to be to the grain size of the matrix and the density, size, and distribution of σ precipitates.

V-4 General Discussion

Some general conclusions can be drawn from this study:

(a) It is clear that Nb_5Ge_3 precipitates, finely dispersed as 100-1000 Å particles, would act as effective pinning centers for vortices in the mixed state. This would explain the initial rise in J_c with second-phase concentration.

(b) The tendency observed in the micrographs for clumping of second-phase precipitates in high-Nb_5Ge_3 content samples, would also explain the saturation of J_c at the higher levels of σ-phase concentration.

(c) The tendency for the A-15 grain size to become more refined, both with decreasing deposition temperature and with increasing Nb_5Ge_3, would also lend support to the idea that grain boundaries are a strong source of pinning. The Nb_5Ge_3 precipitates, thus act both as a primary source of pinning within the grains and secondarily, to limit grain growth and provide a higher density of grain boundaries.

Some unanswered questions posed by this study are:

(a) The unidentified "tweed" structure particles may contribute to effective pinning, but their concentration does not seem to be correlated with any of the process variables.

(b) In some samples the apparent concentration of Nb_5Ge_3 inferred from the micrographs is much higher than that determined by comparison of x-ray peaks. This may reflect a lack of material uniformity for these samples, which were deposited in the horizontal reactor.

(c) The strain contrast noted above appears around Nb_5Ge_3 particles within the A-15 grains and may indicate that the CTE mismatch between Nb_3Ge and Nb_5Ge_3 is placing the Nb_3Ge under strain. This would tend to lower T_c locally and may be related to the 3-5 K difference between T_c and T_c*.

The TEM study has confirmed and elucidated the role of Nb_5Ge_3 in enhancing J_c. It should be pursued further in order to clear up some of the unanswered questions once more uniform material is produced in the moving tape apparatus.

VI. REFERENCES

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3. Thompson, J. D., Maley, M. P., and Newkirk, L. R., "Effect of Second Phase Precipitates and Deposition Temperatures on the Hysteretic Losses in CVD-Prepared Nb_3Ge," Applied Physics Letters, Vol. 30, No. 4, 1977, pp. 190-192.

4. Thompson, J. D., Maley, M. P., Newkirk, L. R., Valencia, F. A., "Measurements of Low Hysteretic Losses in CVD Prepared Nb_3Ge," Physics Letters A57, 351 (1976).

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VII. PRESENTATIONS AND PUBLICATIONS

1. Newkirk, L. R., Valencia, F. A., Carlson, R. V., Maley, M. P., and Thompson, J. D., "Fabrication of Long Uniform Nb_3Ge Tapes and Tubes by Chemical Vapor Deposition," abstract submitted for October meeting of AIME.

2. Hull, G. W. and Newkirk, L. R., "Thermal Expansivity of Nb_3Ge," submitted to Materials Research Bulletin.

VIII. INTERACTIONS AND COLLABORATIONS

The collaboration with A. I. Braginski of Westinghouse Corporation has continued during this quarter. Braginski participated in discussions and joint experiments during two-day visits in April and in June.

IX. PERSONNEL

L. R. Newkirk and F. A. Valencia are the principal investigators producing and improving Nb_3Ge. L. R. Newkirk, F. A. Valencia, J. D. Thompson and E. G. Szklarz are developing the long-sample apparatus. M. P. Maley and J. D. Thompson are responsible for ac-loss and inductive T_c measurements. Self-field critical currents are determined by R. J. Bartlett and R. V. Carlson. The TEM study was performed by T. E. Mitchell. All the activities are carried out in close cooperation with the staff of the LASL dc SPTL project and the LASL Superconducting Materials Working Group.