DEVELOPMENT OF Nb_3Sn CONDUCTOR
FOR
AC SUPERCONDUCTING POWER TRANSMISSION CABLES

FINAL REPORT

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TABLE OF CONTENTS

	List of Tables	ii
	List of Figures	iii
	Acknowledgements	iv
	Abstract	v
<u>Section</u>		<u>Page</u>
1.0	SUMMARY	
	1.1 Study Objectives	1-1
	1.2 Study Results	1-2
	1.3 Future Work	1-3
2.0	INTRODUCTION	2-1
3.0	STATE-OF-THE-ART REVIEW AND TECHNICAL APPROACH	
	3.1 The Technical Approach	3-2
	3.2 AC Loss Measurements	3-6
4.0	INHIBITION OF FORMATION: INVESTIGATION OF TIN COATING PARAMETERS	
	4.1 Experimental	4-1
	4.2 Results	4-3
	4.3 Summary	4-21
5.0	REMOVAL: DEVELOPMENT OF A PROCESS FOR SURFACE REFINEMENT	
	5.1 Experimental	5-3
	5.2 Results	5-4
	5.3 Preparation of Sample Tapes	5-16
	5.4 Summary	5-23
6.0	FUTURE RESEARCH AND DEVELOPMENT	6-1
<u>Appendices</u>		
A	SPECIFICATIONS FOR EXPERIMENTAL SPECIMENS	
B	LOSS MEASUREMENTS - OPERATION OF WATTMETER AND CHARACTERIZATION OF ACCURACY	
C	REFERENCES	

LIST OF TABLES

<u>Table</u>	<u>Title</u>	<u>Page</u>
IV-1	AC Loss and Microstructural Data for Nb ₃ Sn Produced with 100% Sn Coatings	4-6
IV-2	AC Loss and Microstructural Data for Nb ₃ Sn Tapes Produced with Sn-Cu Coatings	4-9
IV-3	AC Loss and Microstructural Data for Nb ₃ Sn Tapes Produced with Sn-Pb Coatings	4-11
IV-4	AC Loss and Microstructural Data for Nb ₃ Sn Tapes Produced with Various Tin Alloy Coatings	4-17
IV-5	AC Loss and Microstructural Data for Nb ₃ Sn Tapes Produced in Supplementary Experiments with Tin Alloy Coatings	4-20
V-1	AC Loss Data for Nb ₃ Sn Tapes Treated by Etching (Experiment 75013.9)	5-5
V-2	AC Loss Data for Nb ₃ Sn Tapes Treated by Etching and Retinning (Experiment 75013C6)	5-11
V-3	AC Loss Data for Nb ₃ Sn Tapes Treated by Etching and Retinning (Experiment 76001.1)	5-12
V-4	AC Loss Data and Critical Current Data for Nb ₃ Sn Tapes Treated by Retinning (Experiment 76003.5)	5-15
V-5	AC Loss and Critical Current Data for Deliverable Experimental Specimens - Qualification Test	5-19
V-6	AC Loss and Critical Current Data for Deliverable Experimental Specimens - Long Length Processing	5-20
B-1	Wattmeter Multiplier Characteristics	B-6
B-2	Summary of Wattmeter Errors and Correction	B-11
B-3	E Probe Wire Size vs. Eddy Current Errors	B-13
B-4	Power vs. Axial Movement of the Probe	B-14
B-5	Power vs. Rotation - Before Improvements	B-13
B-6	Power vs. Rotation - After Improvements	B-16
B-7	E Probe Width vs. Loss in 1/2 Inch Wide Sample	B-16
B-8	Repeatability and Sample Degradation	B-17

LIST OF FIGURES

<u>Figure</u>	<u>Caption</u>	<u>Page</u>
IV-1	Characteristic Microstructure for Nb ₃ Sn Samples	4-5
IV-2	Unalloyed Sn	4-7
IV-3	Sn-Cu Coatings	4-10
IV-4	Sn-Pb Coatings	4-12
IV-5	Sn-4.74 wt. % Pb Coating	4-14
IV-6	Sn-16.7 wt. % Pb	4-15
IV-7	Various Sn Alloy Coatings	4-18
V-1	Etched Tape Samples (Experiment 7513.9)	5-6
V-2	Etched Nb ₃ Sn Layer (Experiment 7513.9)	5-8
V-3	Etched Nb ₃ Sn (Experiment 7513.13)	5-9
V-4	Deliverable Experimental Specimens (762.25)	5-21
B-1	AC Loss Facility Schematic	B-5
B-2	Uniformity of Superconducting Solenoid @ 1600 gauss Central Field	B-10
B-3	Comparison of AC Loss Measurements at IGC and BNL	B-20

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ABSTRACT

The experimental studies performed under this contract comprised investigation of two principal approaches to achieving very low levels of ac loss in Nb_3Sn produced by the liquid diffusion process:

- I. Inhibition of the formation of coarse structured Nb_3Sn surface layers.
- II. Surface refinement by removal of coarse structured Nb_3Sn surface layers.

The results of these investigations are reported in detail.

It was found that ac losses increased directly and sensitively with Sn loading, whereas formation of the coarse surface layer responded limitedly and sluggishly to this parameter. No quantitative correlation was identified between losses and the observed thickness of the coarse structure. Although the effect of coating composition on losses was apparent in some samples, compositional influences tended to be obscured by the predominantly regulatory role of the Sn loading parameter. Nb_3Sn formation under "Sn limited" reaction conditions appeared as the only useful guideline as inferred from the data for achievement of low loss Nb_3Sn product.

In contrast, the investigation focussed upon surface refinement methods which led to a viable and attractive method for achieving low losses in Nb_3Sn tapes, produced by the liquid diffusion process. This method, which was developed, involved a supplementary treatment of Nb_3Sn tape performed after completion of the diffusion heat treatment step in accordance with standard procedure. The supplementary process comprised an etching sequence followed by re-application of Sn; the latter operation restores solderability for the subsequent fabrication of laminated conductor and, under some conditions, contributes to the reduction of ac losses.

The process demonstrated reliability and uniformly successful results in both the investigative experiments and in the preparation of deliverable sample tapes. The treated product is characterized by ac losses which approximate the present target specification for ac transmission cables: $10 \mu\text{W}/\text{cm}^2$ at 500 rms A/cm and 4.2K. Technical requirements for additional research and development have been identified.

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1.0 SUMMARY

Intermagnetics General Corporation (IGC), under contract to the United States Energy Research and Development Administration (Contract E[11-1]-2549), undertook a study directed towards optimizing the superconducting properties of Nb_3Sn in low magnetic fields for use in ac power transmission cables. The increasing demand for energy in the United States makes such a study very timely, since underground superconducting cables are attractive candidates for handling the level of power anticipated in the future; the most likely candidate for a superconducting ac cable has been identified as Nb_3Sn .

1.1 Study Objectives

IGC's efforts in this investigation have included:

- A state-of-the-art review, focusing on the extensive studies performed by the Power Transmission Project at Brookhaven National Laboratory (BNL), which have delineated both the strengths and deficiencies of the available Nb_3Sn tape superconductors.
- Process Studies of Liquid Diffusion Nb_3Sn Tape. To optimize Nb_3Sn for use in ac cables, the coarse surface layer of the tape had to be eliminated or extensively reduced, without loss of critical current or reduction of critical temperature. The target level for surface losses was set at $10\text{--}20\mu\text{ W/cm}^2$, or lower, which is significantly less than the losses measured on untreated surfaces. Experimental work was performed to correlate selected metallurgical variables and process modifications with the microstructure and topography of the Nb_3Sn surface layer and the ac losses. Two basic approaches were investigated:
 - Inhibition of the formation of coarse structured Nb_3Sn surface layers.
 - Surface refinement by removal of the coarse structured surface layers.

- Assembly of Test Equipment and Performance of ac Loss Measurements. The ac loss levels of tape samples were measured, using "electronic wattmeter technique" developed at Brookhaven.
- Fabrication of Experimental Specimens of the Conductor to Meet Target Specifications*. The samples were delivered to Brookhaven for independent analysis.
- Plans for Future Development and Manufacturing Technology Efforts.

1.2 Study Results

AC losses were significantly reduced and near-target loss levels of $10 \mu\text{W}/\text{cm}^2$ were achieved on selected samples. The results of the investigation of the first approach (inhibition of coarse structured surface layer formation) were somewhat tentative.

This study has shown that ac losses increased directly and sensitively with Sn loading, yet the formation of the coarse surface layer was only loosely correlated with this parameter. No quantitative correlation was found between losses and the observed thickness of the coarse structure. Although the effect of coating composition on losses was apparent in some samples, compositional influences tended to be obscured by the predominantly regulatory role of the Sn loading parameter. Nb_3Sn formation under "Sn limited" reaction conditions appeared as the only guideline suggested by the data for achievement of low surface losses.

In contrast, the removal of the surface layers and surface smoothing by chemical means extensively reduced the losses in Nb_3Sn tapes produced by the liquid diffusion process. The method, a supplementary treatment of Nb_3Sn tape after reaction, provided reliable and uniformly successful results. The treated

*See Appendix A

product is characterized by ac losses which satisfy the present target specification for ac transmission cables: $10 \mu\text{W}/\text{cm}^2$ at 500 rms A/cm and 4.2 K.

1.3 Future Work

This program has demonstrated that ac losses in Nb_3Sn can be reduced to the target range; future research and development will investigate those factors found limiting and will extend and refine the processes used in this project for application to commercial production. As outlined in more detail in Section VI, the results of this study suggest that additional investigations be carried out in the following areas:

- Thicker Nb_3Sn Layers. The production of transmission line conductor will require thicker Nb_3Sn layers, which will necessitate the use of thicker Nb-1 Zr starting foils in the liquid diffusion process.
- Effect of Retinning. The significant reduction in ac loss which has been achieved by retinning "as heat treated" tapes without etching is not well understood, and needs to be studied further. Reconsideration of the kind of Nb_3Sn tape used, the formulation of the etchant, and the use of 100% Sn in retinning, particularly with regard to mutual interaction, is required in order to achieve process optimization.
- Continuous Processing. As longer lengths of the product are prepared, process control must accommodate the changes of attack rate which can be expected to result from the accumulation of reaction products in the etch bath.
- Improved Lamination. Substantial improvements are required in the lamination process in order to satisfy the requirements of this demanding application.
- Quality Control. Pilot plant design and quality control planning are two areas to be developed.
- AC Loss Measurements. Problems which were encountered in the measurements of ac losses must be resolved.

2.0 INTRODUCTION

The continuously increasing demand for electrical power in the United States will require vastly more advanced machinery and apparatus than is available today. To accommodate the power generation rate of 8500-9000 billion kWh which is forecast for the year 2000 (a level almost six times greater than the 1974 rate), new efficient generators, possibly of radical design with capacities between 2000-8000 megawatts or higher, will be needed. Consistent with these levels of power generation, transmission lines of capacities of 2-5 GVA will be required to feed urban centers, and interties between regional pools with short circuit capacities of up to 10 GVA may be needed⁽¹⁾. It is doubtful that conventional technology using overhead lines can be extended to capacities of these levels, and it is also doubtful that sufficient land could be made available to such overhead power lines in the unlikely event that conventional technology can be expanded to accommodate these increases.

The use of conventional underground cables would solve the land use problem; however, these cables are limited in their capacity by the associated heating of the surrounding soil. A strong case, on the other hand, can be made for the underground superconducting cables, since the properties of superconductors now available suggest that an underground line capable of multi-gigawatt capacity is technically feasible. Such a superconducting cable:

- could feed urban centers with a very small right-of-way.
- could accommodate surge impedance loading.
- is independent of local soil conditions.
- offers a "critical length" of several miles.
- can probably carry heavy fault currents without stripping.
- can continue to carry rated current immediately after a fault.

The most likely conductor candidate for superconductive ac power transmission cables has been identified as Nb_3Sn ⁽²⁾. While it is likely that over the next decade newer and better superconductors may be discovered and developed for ac cable applications, it is quite clear that on a 3-5 year time scale, Nb_3Sn is the only candidate material that to date

- is sufficiently understood and developed

- is manufactured reproducibly in commercial quantities and used for device applications.
- has superconducting properties capable of meeting the demanding technical performance requirements of ac cables.

However, until recently, Nb₃Sn development programs have been devoted to the improvement of its superconducting properties in high magnetic fields; ac cables, on the other hand, involve low fields. Thus, to optimize the superconducting properties of Nb₃Sn for use in ac cables, Intermagnetics General Corporation (IGC), under contract to the United States Energy Research and Development Administration (ERDA), undertook a research effort to delineate and improve the performance characteristics of the conductor in low magnetic fields.

IGC's work has essentially consisted of an assessment of methods for improving Nb₃Sn tapes for use in ac cables and implementation of selected research and development approaches to provide such optimized tape conductors. More specifically, IGC has performed:

- A state-of-the-art review.
- Process studies of liquid diffusion Nb₃Sn tape.
- Assembly of test equipment and performance of ac loss measurements.
- Fabrication of experimental specimens of the conductor to meet target specifications.*
- Plans for future development and manufacturing technology efforts.

This work, in full conformance with the Work Statement specified for Contract E(11-1)-2549 and subsequently amended,⁽³⁾ is reported in the Sections that follow.

*See Appendix A.

3.0 STATE-OF-THE-ART REVIEW AND TECHNICAL APPROACH

As preliminary work for the study and implementation of methods for improving Nb_3Sn for use in ac cables, IGC undertook a state-of-the-art review and literature search, relying greatly on the extensive work performed by Brookhaven National Laboratory on the strengths and deficiencies of the available Nb_3Sn tape superconductors.⁽⁴⁾ With respect to "liquid diffusion process" Nb_3Sn (as typified by the commercial superconductors manufactured by IGC), the critical capabilities and possible limitations of the conductor prior to this program are summarized as follows:

- A detailed investigation⁽⁵⁾ of ac critical current properties concluded that for cable designs with 500 rms A/cm normal rating at temperatures around 8 K, large overloads could be handled without the conductor going normal. Quench currents in excess of 5000 rms A/cm (60 Hz, 4.2 K) were observed. The existent critical current capability was, therefore, shown to be satisfactory.
- An analysis⁽⁶⁾ of the source of losses in commercial tapes showed that the Pb-Sn solders used in cladding the superconductor gave rise to high levels of hysteretic loss, which exceeded those of the Nb_3Sn itself in the low field region of interest. These losses, which are expected to be largely avoidable by appropriate control of the cladding procedure, had previously obscured the actual level of loss associated with the Nb_3Sn per se.
- The loss characteristics of unclad Nb_3Sn tapes had also been investigated in considerable detail.⁽⁷⁾ Although extensive variability was observed, the losses for commercial tapes were predominantly much above allowable limits. The losses determined for IGC's samples ranged from about $60\text{--}120 \mu\text{W}/\text{cm}^2$ (500 rms A/cm, 60 Hz, 4.2 K) as compared to the $10 \mu\text{W}/\text{cm}^2$ target requirement. These investigations showed that the magnitude of the ac loss related to the degree of surface roughness.

- High J_c forms of Nb_3Sn produced by the liquid diffusion process are generally characterized by a coarse structured surface layer of significant thickness. Although this characteristic had been generally recognized, its pertinence to ac loss contribution was elucidated by the BNL studies.⁽⁴⁾

This state-of-the-art analysis confirmed the necessity for eliminating or extensively reducing the coarse surface layer of Nb_3Sn , without reducing critical current and critical temperature.

Further research indicated that the two approaches chosen to accomplish this objective were also justified. Studies of the coarse surface layer of Nb_3Sn and attempts to remove it through some form of polishing process demonstrated the necessity for:

- 1) The inhibition of the formation of the coarse surface layer by changes in the procedures and control of the liquid diffusion process, or
- 2) The removal of the layer from the usual form of Nb_3Sn by a suitable supplementary process.

3.1 The Technical Approach

1) Inhibition of Formation

Concern with the coarse structured surface layer of Nb_3Sn usually appearing in the product of the liquid diffusion process is not new. The research efforts of the late 1960's which developed the present day superconductor for high field dc applications observed the zone of degraded microstructure and devoted considerable investigation to both understanding and eliminating the defect. Indirect evidence indicated that this nondense stratum did not contribute to current transport because of low J_c and/or discontinuity effects. On this basis, both Nb utilization and volume efficiency of the superconductor were degraded. A puzzling background problem in this work was that formation of the degraded microstructure was mainly observed under a

process circumstance contributing dramatically beneficial effects with respect to critical current capability and reaction kinetics (e.g., the use of internally oxidized Nb-Zr alloy substrates and the addition of Cu). The net effect, consequently, was that superior superconductors were achieved despite the parasitic microstructural form.

Benz⁽⁸⁾ investigated the problem by experiments producing Nb₃Sn on Sn coated Nb-1 Zr foil and interpreted the coarse phase observed in terms of two competing processes:

- a dissolving process whereby the contacting layer of liquid tin dissolves niobium or any of its intermetallic compounds in order to come to a saturated niobium concentration, as would be indicated by the liquidus curve of the phase diagram, and
- a diffusing process whereby primarily tin diffuses through Nb₃Sn to form more Nb₃Sn at the niobium-Nb₃Sn interface. The nondense surface layer is formed whenever the diffusing process forms significant amounts of Nb₃Sn before the dissolving process is complete. The dissolving process preferentially etches away the grain boundary regions of the newly formed Nb₃Sn grains, leaving the faulty structure.

A study by Old and MacPhail⁽⁹⁾ utilized a somewhat bulkier diffusion couple to produce Nb₃Sn on Nb rods (0.125 in diameter). The conclusions reported by these authors differed little from those of Benz. They deduced that Nb₃Sn forms partly by diffusion and partly by a solution/deposition mechanism which depends on thermal gradient mass transfer; the rough surface layer was considered to have been formed by the latter process mode. A further conclusion from this research was that because of the solution/deposition mechanism, the use of minimal quantities of Sn would tend to minimize formation of the coarse structured modification.

Earlier unpublished work⁽¹⁰⁾ also identified the importance of Sn quantity relative to the appearance of the nondense phase. Certain experimental samples were produced with Nb-Zr foils, which had been subjected to surface deformation. Dramatic differentiation of the effects of Sn quantity variations were exhibited by the microstructure of the Nb₃Sn subsequently produced. In knurled tapes having valley contour locations, Nb₃Sn formation occurred in Sn puddles that were characterized by copious occurrence of the coarse structured modification. Conversely, hill top contours, which were devoid of excess Sn, were observed to be fully free of the nondense structure. Other experiments of that work suggested that the composition of the tin coating could also influence formation of the coarse structured layer (e.g., Pb doping of the Sn appeared to be inhibitory). This earlier program of research on liquid diffusion process tapes also devoted substantial and comprehensive study to process aspects other than those relating to the tin coating (e.g., substrate materials and preparatory processing). No evidence was found for a regulating role by other process elements with respect to formation of the coarse structured layer.

The prior work in the subject thus presented a strongly persuasive view that any system for inhibiting formation of the ac loss-contributing coarse structured surface layer would most likely provide such control within the parameters of the tin coating operation. Although much study had been devoted to the system, it was considered that the work to be done by IGC would gain a strong advantage from the use of loss measurements as the primary data basis. Prior work had been limited by virtually complete dependence upon metallographic observations and high magnetic field measurements. In addition to the technique problems associated with very thin layers characterized by an extreme divergence of hardness (Sn versus Nb₃Sn), uncertainties arise because of the extremely limited sampling, which is inherent in the observation of a microstructural conformation that exhibits statistical variation in the macro sample.

Within the context of this contract, IGC undertook a study of two important parameters in the tin coating operation as the first phase of this program. These variables were the composition and quantity of the tin alloy applied to the surface of the substrate niobium. The experimental work is reported under Section IV.

2) Removal

Although removal of the surface layer by some form of polishing process was included in the initial planning of the current program, a greatly advanced starting point was contributed by the very exciting results achieved by Bussiere and Suenaga^(11,12) at about the time the present experimental work was initiated. Thick layers of Nb_3Sn (30-90 μm) were produced by the liquid diffusion process on rod specimens (3 mm diameter). Initially high ac losses in the "as heat treated" condition were reduced to about $1 \mu\text{W}/\text{cm}^2$ (60 Hz, 4.2 K) by fine mechanical polishing, electro-polishing or chemical etching of the surface. This reduction in the losses was attributed to removal of the coarse structured surface layer.

This prior work had thus demonstrated feasibility for an attractive approach to achieving low losses in a conventional form of Nb_3Sn . Therefore, the ultimate objective in the present work was to develop a practical operating process which could perform the required removal of material on the comparatively fragile superconductor tapes required for the power transmission cable. Bussiere and Suenaga had achieved the lowest losses by the use of procedures based on mechanical polishing, and although some consideration was devoted to possible adaptations of this method, the problems of fragility and some lack of flatness in the tapes were viewed as prohibitive. Chemical or electromechanical processing, on the other hand, appeared to provide a viable operating basis. This optimism was, in part, a product of IGC's successful experience in the development of a process system for producing a multifilamentary matrix in Nb_3Sn tape by chemical milling⁽¹³⁾.

3.2 AC Loss Measurements

The alternating field losses in tape superconductors, which have had such an essential role in the present attempt to optimize Nb_3Sn for use in ac cables, pertain to the losses induced in the presence of an alternating field applied parallel to the broad face of the conductor. The loss measurements used in this work were made by the electronic wattmeter technique, which has been described previously^(6,7,14) and which is becoming well known.

The Poynting vector $\mathbf{E} \times \mathbf{H}$ (in which $\mathbf{E}$ and $\mathbf{H}$ are the instantaneous values of the electric and magnetic field vectors respectively) on the surface of the tape contains the loss formation. Probe coils were provided to give the instantaneous values of $\mathbf{E}$ and $\mathbf{H}$. The wattmeter yielded the time-average of the product $\mathbf{E} \times \mathbf{H}$ and gave the steady state loss directly.

The facility used in making the present measurements was specifically designed in conformance with the system in use at Brookhaven National Laboratory in order to facilitate the comparison of loss data; the wattmeter itself was a component constructed under the direction of the BNL staff.

The possible sources of error in the wattmeter technique were examined in order to provide an estimate of the degree of accuracy expected in these measurements, since errors may be introduced by the wattmeter itself. Additional variation in measured loss is due to sample and probe mounting. In general, the accuracy of the ac loss measurements presented here as a function of loss level were expected to lie in the ranges tabulated below:

EXPECTED ACCURACY

<u>Loss ($\mu\text{W}/\text{cm}^2$)</u>	<u>% Error</u>
5-20	+30 -10
20-100	± 10
>100	± 5

A more detailed description of the wattmeter together with a discussion of its operation and accuracy are presented under Appendix B.

4.0 INHIBITION OF FORMATION: INVESTIGATION OF TIN COATING PARAMETERS

This phase included a study of two critical parameters in the tin coating operation of the "liquid diffusion process"; these variables were (1) the quantity and (2) the composition of the tin alloy applied as a surface coating to the niobium substrate foil. The objective of the investigation was to determine whether suitable adjustment of these variables could provide a basis for process control, which would eliminate or extensively reduce the formation of the coarse structured surface layer in the Nb_3Sn product. As previously discussed, such modification of the microstructure would be expected to substantially lower ac losses.

4.1 Experimental

The tin coating compositions considered in this series of experiments included unalloyed tin, and alloys of tin with copper, lead, antimony, bismuth and indium. The alloys were prepared from pure constituent metals (99.98% or purer) by co-melting under argon in the quartz crucible of the tin coating apparatus. Stirring in combination with a 1 hour soak at 1050 C insured homogenization.

The second variable, the quantity of tin alloy coating, was controlled indirectly by varying the velocity (from 0.5 to 4.3 m/min.) at which the tape was passed through the melt. The tin loading actually achieved in any particular sample was determined as the weight of coating per unit length of foil; these data were obtained with the use of an analytical balance on approximately 3 m long tapes. Average tin loading, as determined from the data for an initial group of nine experiments, was found to increase linearly with tape velocity over the range considered. Although the data were characterized by appreciable scatter (average deviation $\pm 12\%$), the method did provide a graded series of Sn loadings between the two levels which were of specific interest:

- Substantially less Sn than required to sustain the reaction of available Nb for the imposed conditions of temperature and time, thus providing a "Sn limiting" reaction condition.

- Substantially more Sn than required to sustain the reaction of available Nb for the imposed conditions of temperature and time, thus providing a "Sn excess" or "time limiting" reaction condition.

The quantity of tin coating (in addition to the composition of the coating) was the only variable which was adjusted in this series of experiments; the operating variables of the liquid diffusion process were held constant. Niobium substrates (internally oxidized, nominal 1 wt. % Zr, about 25 μm thick) were used "as rolled". The tinning process was performed at 1050 C under an argon atmosphere, as was the diffusion heat treatment, with a single exception: in the latter, the use of a Sn-16.7% Pb alloy sufficiently retarded reaction kinetics to require an increase in the diffusion temperature to 1150 C in order to sustain practical operation.

A standardized procedure was employed in the diffusion heat treatment of the tin coated niobium substrates to form the Nb_3Sn phase. Trial samples for each coating composition were heat treated at a series of times utilizing the variate having the highest tin loading (4.3 m/min.). The extent of reaction occurring in these time trial samples was determined by metallographic examination, and on the basis of these results a time was selected for which the extent of reaction allowed a core of unreacted niobium about 7-9 μm thick. Samples of all the tin loading variates of that composition group were then heat treated at the selected time. This process produced sample groups characterized by a Sn-limited forming reaction for Nb_3Sn at the lowest loading (0.5 m/min.) and a Sn-excess or time limited reaction at the highest loading (4.3 m/min.) in all cases; intermediate loadings provided varying degrees of Sn-insufficiency or excess relative to the time-regulated reaction.

The ac losses were determined for each variate by the methods described in the preceeding section. Surface coarseness was evaluated by examination of transverse sections of each variate by optical microscopy; thorough measurements were made of the microstructural features of interest with the use of a filar micrometer eyepiece.

4.2 Results

The experimental results for the study of tin coating parameters are summarized in Tables IV-1 through IV-5 and Figures IV-1 through IV-7. The tables list the data for ac loss and for the extent of the coarse structured surface layer as a function of the composition and loading variables. A comment on the nature of these data and the inferences which are enabled:

- Composition (wt %): The concentration of additive metal in the tin alloy coatings was calculated from the weights of constituent metals used for preparation of the melt.
- Sn Loading (mg/cm²): As previously noted, gross loading was determined by measurement of the weight gain resulting from application of the coating to 3-10 m long tape specimens; therefore, an average value of loading is implied. The data as listed in the tables have been normalized in terms of the elemental Sn content of the coating (calculated from gross loading on the basis of the listed composition) in order to make the stoichiometric relationship apparent; the theoretical requirement for Sn in the conversion of Nb to Nb₃Sn is 0.18 mg Sn/cm² per μm of Nb thickness reacted. However, this use of Sn normalized data had the disadvantage of obscuring comparisons of gross alloy loading between runs of different composition.
- Nb Reacted (μm): These data were determined as the difference between the thickness of the unreacted Nb core remaining after reaction (measured in metallographic sections with the use of a filar micrometer eyepiece) and the thickness of the starting foil (determined for the particular length of foil used in the experiment on the basis of weight/dimension/density parameters). The thickness of Nb reacted at the highest Sn loading (i.e., the loading resulting from a tape velocity of 4.27 m/min.) specified the extent of the time limited reaction (1050 C, excess Sn). Examination of the data for lower loadings indicated a general reduction of the extent of reaction. These data thus provide a readily apparent scaling of the degree of Sn limitation imposed on the Nb₃Sn forming reaction by the lower loadings.

- AC Loss ($\mu\text{W}/\text{cm}^2$): The data listed in the tables are for the most part the results of only one determination; however, a group of five of these variates was subjected to retest, and no significant disagreement with the first set of data was found
- Coarse Structured Surface Layer: The listed data pertain to the total for the two reaction layers of the tape with reference to both the measured thickness and the percentage occurrence within the Nb_3Sn phase. A typical structure is illustrated in Figure IV-1.

Unalloyed Sn Coatings

The experimental results for the sample set produced with unalloyed Sn are listed in Table IV-1, which shows ac losses rising steeply with increasing Sn loadings. The loss characteristic for these materials is displayed more extensively in Figure IV-2 as a plot of loss versus surface current density.

The Sn loading required to sustain the Nb_3Sn forming reaction for the time of heat treatment used may be estimated from the observed thickness of Nb reacted under the time-limited condition (tape velocity 4.27 m/min.):

$$13 \mu\text{m} \times 0.18 \frac{\text{mg Sn}/\text{cm}^2}{\mu\text{m Nb reacted}} = 2.34 \text{ mg Sn}/\text{cm}^2.$$

Relative to this requirement, the observed loadings correspond to 88%, 100%, 114% and 274% of stoichiometric Sn respectively for the ascending series of loadings (2.04, 2.36, 2.66, 6.42 mg/cm^2). Thus, the data indicate that a threefold increase of ac loss (8.4 to 26 $\mu\text{W}/\text{cm}^2$) results from a very limited excess of Sn (14%). In contrast, the data for the occurrence of the coarse structured surface layer show no apparent correlation with either loading or ac losses: the variation of layer thickness is quite limited and apparently random.

At the two lower levels of Sn loading the measured ac loss is well within the presently specified limit of acceptability (see Appendix A). Although critical current capability was not determined, high field critical current was estimated to be about 260 A/cm (10 T, dc) based on the data of prior work. Since the ac quench current is generally expected to exceed 10 T critical current by at

Figure IV-1: Characteristic Microstructure for Nb₃Sn Samples. This sample (7513.14) features Sn-16.7 wt. % Cu and excess Sn (2350X).

Table IV-1

AC LOSS AND MICROSTRUCTURAL DATA FOR Nb_3Sn TAPES PRODUCED WITH 100% Sn COATINGS

Tape Velocity (m/min)	Sn Loading (mg/cm ²)	Nb Reacted (μm)	Loss ($\mu\text{W}/\text{cm}^2$)		Coarse Structured Layer	
			at 500 rms A/cm	at 1000 rms A/cm	Thickness (μm)	% of Total Nb_3Sn
0.53	2.04	11	5.9	390	7.1	44
1.07	2.36	13	8.4	540	11	57
2.13	2.66	14	26	850	9.4	40
4.27	6.42	13	51	1050	8.4	38

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Fig. IV-2: Unalloyed Sn. The effect of Sn loading on ac losses is shown for 100% Sn coatings.

- 2.04 mgSn/cm²
- 2.36 mgSn/cm²
- ◇ 2.66 mgSn/cm²
- △ 6.42 mgSn/cm²

least an order of magnitude, acceptability with respect to the target specification for quench current can be predicted (see Appendix A). However, in spite of the acceptable ac loss, both of these samples showed dry, Sn depleted surfaces, which were judged to be unsatisfactory for lamination without supplementary processing to restore solderability.

Sn-Cu Alloy Coatings

The Sn-Cu system was investigated in some detail, as indicated by the results shown in Table IV-2 and Figure IV-3. At the onset of this study, this system was considered to be of great interest because of the substantial benefits it contributes to both more rapid reaction kinetics and enhanced critical current capability. However, the investigation found that the addition of Cu to the tin coating generally increased ac loss. Surprisingly though, the loss increase relative to the losses produced by unalloyed Sn was greatest at the lower levels of concentration and loading; the loss characteristic was not extensively influenced at the conditions at which high losses had been observed in the 100% Sn system (i.e., excess Sn and the higher level of surface current density).

The data for the thickness of the coarse structured surface layer display a generally systematic trend in these experiments: i.e., layer thickness increased with loading. Strangely, these data appear characterized by relatively limited and random variation when viewed as a percent of the Nb_3Sn layer, which has the effect of normalizing the data with respect to the extent of product formation. One might anticipate either a generally constant percentage value reflecting a fixed structural composition or, alternatively, a percentage level which declines with increasing product formation, thus suggesting a relatively fixed amount of coarse structured layer.

Sn-Pb Alloy Coatings

The initial investigation of this system featured 4.7% and 16.7% Pb coatings. As shown by the data in Table IV-3 and Figure IV-4, these experiments provided evidence that the incorporation of Pb into the tin coating produced a

Table IV-2

AC LOSS AND MICROSTRUCTURAL DATA FOR Nb_3Sn TAPES PRODUCED WITH Sn-Cu COATINGS

Cu Content (wt %)	Tape Velocity (m/min)	Sn Loading (mg/cm ²)	Nb Reacted (μm)	Loss ($\mu\text{W}/\text{cm}^2$)		Coarse Structured Layer	
				at 500 rms A/cm	at 1000 rms A/cm	Thickness (μm)	% of Total Nb_3Sn
4.7	0.53	1.32	10	210	1020	6.1	38
	1.07	1.75	13	180	1320	6.9	34
	2.13	3.29	17	94	1100	8.4	32
	4.27	5.02	20	120	1080	15	45
9.1	0.53	1.55	9.1	120	1030	3.8	28
	1.07	1.66	12	80	910	7.6	41
	2.13	3.18	17	74	920	7.1	31
	4.27	5.19	15	98	820	9.4	43
16.7	0.53	1.87	9.7	65	910	6.9	46
	1.07	2.92	12	36	660	6.6	37
	2.13	4.71	20	43	880	11	36
	4.27	5.64	19	120	980	15	46
23.0	0.53	1.53	7.4	56	770	4.3	32
	1.07	2.03	9.4	42	660	3.6	23
	2.13	3.03	12	36	600	5.3	23
	4.27	4.43	17	85	890	4.8	20
28.5	0.53	1.54	7.4	64	990	2.5	20
	1.07	2.01	11	50	680	5.6	29
	2.13	2.60	15	62	690	6.6	28
	4.27	4.90	20	83	860	8.1	25

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Fig. IV-3: Sn-Cu Coatings: The ac loss at 500 rms A/cm is shown as a function of Cu concentration and Sn loading.

Table IV-3

AC LOSS AND MICROSTRUCTURAL DATA FOR Nb₃Sn TAPES PRODUCED WITH Sn-Pb COATINGS

Pb Content (wt %)	Tape Velocity (m/min)	Sn Loading (mg/cm ²)	Nb Reacted (μm)	Loss (μW/cm ²)		Coarse Structured Layer	
				at 500 rms A/cm	at 1000 rms A/cm	Thickness (μm)	% of Total Nb ₃ Sn
0.51	0.53	0.754	11	11	430	5.6	39
	1.07	1.57	12	12	470	6.1	35
	2.13	2.96	14	13	590	7.1	34
	4.27	4.80	17	24	830	10	41
0.99	0.53	1.67	11	8.7	400	3.6	38
	1.07	2.22	11	16	560	4.8	37
	2.13	4.11	14	21	620	7.9	41
	4.27	5.98	17	50	1070	12	49
1.96	0.53	1.81	8.9	10	380	2.5	37
	1.07	2.46	11	17	540	5.6	55
	2.13	3.62	12	17	520	6.1	46
	3.20	3.57	14	23	570	5.6	46
	4.27	5.09	17	62	970	7.4	40
4.74	0.53	2.16	9.7	7.9	350	5.3	50
	1.07	2.26	14	8.0	390	9.4	43
	2.13	3.28	17	18	600	6.1	24
	4.27	5.08	17	20	670	10	42
16.7	0.53	1.65	7.9	5.8	350	4.3	41
	1.07	2.20	9.7	11	400	5.6	39
	2.13	2.85	11	18	560	4.6	28
	4.27	4.52	14	17	710	8.9	41

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significant alteration in loss behavior. Although the measured losses were only equivalent to those of unalloyed tin at the lower levels of loading, the presence of Pb apparently acted to inhibit the extent of increase in losses at the higher tin loadings; these higher tin loadings afford the more practical basis for manufacturing, since more extensive Nb_3Sn formation and higher critical currents are facilitated. This improvement was demonstrated more markedly at the higher current levels. Interestingly, the results for the two concentrations did not differ significantly.

The loss data for these variates are shown in Figures IV-5 and IV-6 for the full range of the measurements (130-1380 rms A/cm). These curves display in part the reduced slope characteristic below 300 rms A/cm described by Bussiere, Garber and Suenaga⁽⁶⁾ relative to Pb-Sn solders. Surprisingly, this slope reduction is absent from the curves for the highest tin loadings of the 4.7% and 16.7% experiments.

On the basis of these intriguing results an additional series of lower Pb concentrations was investigated. Alloy coatings containing more than 5% Pb appeared to be of little interest, since the 4.7% and 16.7% Pb coating had essentially equivalent effects on ac loss. In addition, reaction kinetics had been very substantially retarded by 16.7% Pb, whereas the rate of the Nb_3Sn forming reaction with 4.7% Pb was approximately the same as that for 100% Sn. The results obtained with the nominal 0.5%, 1% and 2% Pb compositions which were chosen are included in Table IV-3 and Figure IV-4.

The loss characteristic determined for the samples produced with the lower Pb alloys does not indicate a continuum or systematic trend relative to initial data for 4.7% Pb, since both the 1% Pb and 2% Pb variates exhibited losses comparable to the loss observed with unalloyed tin for "excess Sn" reaction conditions. The relatively limited depression of loss demonstrated by the 0.5% Pb - "excess Sn" result is considered dubious evidence of an inhibitory effect because of the absence of trend in the overall data pattern. In total, the results indicated that a concentration of about 5 wt. % lead in the tin coating was probably near optimum for any potential usefulness in inhibiting the increase in ac losses at higher tin loadings: no benefit was contributed by a 2% addition, and concentrations much above 5% adversely influenced reaction kinetics.

INTERMAGNETICS

INTERMAGNETIOS

The data for the coarse layer in the Sn-Pb system appear analogous to those for Sn-Cu: the thickness of the layer increased with Sn loading on a generally systematic basis. No trend is apparent when these data are considered as a percent of the total Nb_3Sn product.

The sample tapes produced with Sn-Pb coatings were generally characterized by a somewhat irregular spotted or streaked appearance, which was interpreted as evidence of a non-uniform redistribution of the alloy coating occurring during the diffusion heat treatment; this appearance trait maximized at the low loading and high Pb conditions of the experiment. The sample of predominant interest (4.74% Pb/4.27 m/min.), showed a dark, relatively uniform-appearing surface, but was judged to have partially dewet areas which would prohibit successful lamination in the "as heat treated" condition. This judgment was not confirmed experimentally.

Various Sn Alloy Coatings

Since the investigation of Pb addition to the Sn coating had demonstrated the possibility of reducing the ac losses by such compositional modifications, a limited survey of other additive metals was undertaken. Experiments were successfully completed with nominal 2 and 5 wt. % alloys of Bi, Sb and In. Samples were produced with Sn-2% Al, but the experiment encountered difficulties in the form of a corrosive interaction of the melt with the quartz crucible, which presumably prevented the heat treatment of the sample tapes from accomplishing any significant formation of Nb_3Sn (about 20 minutes at 1125 C).

The results of the experiments with Bi, Sb and In are summarized in Figure IV-7 and Table IV-4. Neither Sb nor In acted to depress the ac losses; in fact, the results with both 2% and 5% Sb coatings showed an apparent elevation of the losses relative to those observed with unalloyed Sn. The losses for the samples produced with the In alloy coatings were similarly high and appeared somewhat insensitive to Sn loading.* Although the use of 2% Bi did not appreciably influence loss behavior, the tapes produced with 4.76% Bi coatings did demonstrate significantly reduced losses at the higher Sn loadings as compared to the results with unalloyed Sn.

*Ambiguous data were obtained with 4.75% In at the standard 0.53 m/min. tape velocity, and the results have been omitted from Table IV-4 and Figure IV-7.

Table IV-4

AC LOSS & MICROSTRUCTURAL DATA FOR Nb₃Sn TAPES PRODUCED WITH VARIOUS TIN ALLOY COATINGS

Additive Metal (wt %)	Tape Velocity (m/min)	Sn Loading (mg/cm ²)	Nb Reacted (μm)	Loss (μW/cm ²)		Coarse Structured Layer	
				at 500 rms A/cm	at 1000 rms A/cm	Thickness (μm)	% of Total Nb ₃ Sn
1.96 Bi	0.53	1.37	8.9	13	370	3.6	50
	1.07	2.31	12	16	530	7.1	54
	2.13	3.37	12	35	630	6.1	48
	3.20	4.88	14	14	700	5.8	56
	4.27	5.27	17	69	1030	8.9	39
4.76 Bi	0.53	1.32	10	7.6	380	5.8	41
	1.07	2.07	11	10	370	5.6	42
	2.13	2.70	12	17	510	5.6	33
	4.27	5.73	20	9.6	370	16	49
1.95 In	0.53	1.71	11	22	600	4.8	59
	1.07	2.21	13	22	670	2.5	53
	2.13	2.88	11	28	810	3.6	44
	3.20	4.18	13	39	940	5.8	47
	4.27	4.95	15	41	930	7.6	48
4.75 In	1.07	2.80	13	63	940	13	60
	2.13	3.48	14	53	930	16	54
	3.20	5.19	16	65	980	14	45
	4.27	5.92	15	78	1110	14	49
1.96 Sb	0.53	1.42	11	16	350	3.0	48
	1.07	1.80	12	18	420	3.0	40
	2.13	3.29	14	69	730	5.6	35
	3.20	3.92	14	83	780	6.6	35
	4.27	5.14	14	130	1030	9.1	40
4.76 Sb	0.53	1.66	9.7	17	240	2.5	40
	1.07	2.38	12	24	330	4.6	39
	2.13	2.53	12	46	460	4.3	35
	3.20	4.08	16	62	540	8.1	43
	4.27	4.74	15	76	670	6.1	34

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Fig. IV-7: Various Sn Alloy Coatings. The ac loss at 500 rms A/cm is shown as a function of additive metal concentration and Sn loading.

The measured losses for the 4.76% Bi sample having the highest Sn loading (5.73 mg/cm^2 , which corresponds to 159% of the stoichiometric requirement) appeared significantly superior to the results achieved with a comparable concentration of Pb (9.6 versus $20 \text{ } \mu\text{W/cm}^2$) at a similar "excess Sn" (166%) reaction condition. However, the surface of this sample showed apparent evidence of irregular flow patterns in the residual Sn layer and partially dewet areas, which would probably prevent lamination "as heat treated". The reaction kinetics for Nb_3Sn formation were not significantly altered by the Bi additions used. The overall data for the coarse structured layer in this series of experiments again demonstrate the generally consistent increase of layer thickness with Sn loading. However, although general qualitative correlation is apparent in that both the coarse structured layer and ac losses increased with Sn loading, the relationship is quite inexact.

Supplementary Experiments

The experiments of this series were follow-up investigations of some of the results reported on in the preceding sections. The principal objective was to re-examine the apparently beneficial influence of Pb and Bi additions on ac losses which had been shown by the rather sparse initial data.

An early experiment investigated a combination of Cu and Pb additions to the tin coating (Sn - 15.9 wt. % Cu - 4.1 wt. % Pb) in the hope that the incorporation of Pb would reduce the high losses resulting from the otherwise beneficial copper additions. The results (see Table IV-5 and Figure IV-4) demonstrated that the effect of Cu predominated; the high loss levels observed were essentially similar to the results with Sn-Cu binary alloys.

Another experiment re-examined the loss behavior resulting from a nominal 5% Pb coating reacted in the presence of excess Sn (i.e., the conditions initially showing a beneficial effect). The experiment featured foil surfaces both "as rolled" and "knurled"; the knurled surface was introduced with the objective of maintaining a more uniform distribution of the surplus tin in order to provide a solderable surface "as heat treated". The results, which are listed under Table IV-5, proved disappointing. The favorable loss characteristic of the earlier experiment was not reproduced: both variates showed high levels of loss comparable to these observed with pure Sn. Although the knurled foil

Table IV-5

AC LOSS AND MICROSTRUCTURAL DATA FOR Nb₃Sn TAPES PRODUCED IN SUPPLEMENTARY EXPERIMENTS WITH TIN ALLOY COATINGS

Additive Metal (wt %)	Tape Velocity (m/min)	Sn Loading (mg/cm ²)	Nb Reacted (μm)	Loss (μW/cm ²)		Coarse Structured Layer	
				at 500 rms A/cm	at 1000 rms A/cm	Thickness (μm)	% of Total Nb ₃ Sn
15.9 Cu & 4.1 Pb	0.53	1.45	9.7	160	1030	4.8	35
	1.07	1.62	13	100	1100	5.3	30
	2.13	3.18	17	35	640	7.9	30
	4.27	5.06	18	88	820	7.6	28
4.76 Pb	4.27 (a)	5.08	16	38	910	8.9	49
	(b)	5.31	18	54	1040	10	50

Note: (a) Foil surface "as rolled" (b) Foil surface "knurled"

4.76 Pb	4.27	5.60	15	29	610	3.8	23
4.75 Bi	4.27	6.50	16	36	680	3.8	18

produced an apparently uniformly "tinned" surface suitable for lamination, the measured losses were about 40% higher than those of the "as rolled" variate. The increased losses of the knurled sample are thought not to have been caused by the knurl per se, but rather by the fact that the knurl caused a relatively higher Sn loading to be uniformly sustained over the surface of the sample.

Final experiments in this study repeated the runs with both Pb and Bi alloys (nominal 5 wt. %) at the excess Sn condition. In both instances, the ac losses for the tapes (see Table IV-5) proved substantially higher than the favorable results observed in the earlier experiments of the study. It might be noted that the loss data for these experiments were determined on triplicate samples; overall deviation from the average was about $\pm 3 \mu\text{W}/\text{cm}^2$ at 500 rms A/cm.

4.3 Summary

The results of this study, which has considered the effect of the quantity and composition of the tin coating on the ac losses and coarse structured surface layer of Nb_3Sn tapes produced by the liquid diffusion process, are somewhat difficult to summarize. Although certain dominant traits appeared to regulate the behavior of the system, exceptions and incomplete correspondence to the rule tended to render most general statements imperfect. The following generalizations are stated with the acknowledgment that they represent a best judgment of the predominant characteristics shown by the experimental data. For the purpose of the present discussion, reference to "losses" will infer the values determined at 500 rms A/cm, which is the standard surface current density of the target specification.

1. Losses respond directly and sensitively to Sn loading. This is demonstrated most markedly by the data for 100% Sn, for which a 3X increase in loading resulted in a 9X increase in the loss property. The correlation is generally apparent in the data for all the compositional systems considered in this study with the exception of Cu alloys, which displayed essentially nonsystematic behavior.

2. The thickness of the coarse structured Nb_3Sn surface layer adjacent to the Sn interface also showed a general tendency to increase with Sn loading. This trait was apparent in all comparisons between the results for minimum loading (Sn limited reactions) and maximum loading (excess Sn), but was not consistently displayed through the range of intermediate loadings. The correlation was absent in the data for 100% Sn.

Some amount of coarse structured layer was observed in all samples of the study: no variate suggested the possibility of conditions which might eliminate the malformed structure. A relatively limited range of variation was observed, with layer thickness typically varying from about 4 μm to 10 μm between the conditions of minimum and maximum Sn loading. No systematic trend was observed in the formation of coarse layer relative to coating composition.

3. Since both ac loss and the thickness of the coarse structured layer increased with Sn loading, it is apparent that losses must increase with the thickness of the coarse layer. This cross correlation, however, is illustrated only generally by the experimental data of the present work. The results in Table IV-3 for 4.74% Pb are illustrative: an increase in losses from 8 to 20 $\mu\text{W}/\text{cm}^2$ (500 rms A/cm) is associated with an increase of 5 to 10 μm in the thickness of the coarse layer between the extremes of the Sn loading series; at the same time, the data for intermediate loadings fail to show continuity in the trend and negate the quantitative correlation.

A number of factors might possibly be involved in this failure to achieve quantitative correlation. For example, the small magnitude of structural change tends to allow any experimental scatter to obscure systematic effects; the data may lack representativeness due to the smallness of the sample in the microscopic determination of layer thickness. However, the most likely implication is thought to be that features other than the coarse structured layer as

presently identified are also influencing the losses. Such features might be different kinds of malformed structure within the layer, which have different degrees of influence on losses, or an additional substructure condition not visible by optical microscopy.

4. The relative effects on the ac loss property of the various alloying additions to the tin coating proved difficult to differentiate because of the prevailing and dominant influence of Sn loading. Most of the experimental data tended to reflect a behavior not too different from that of 100% Sn; Cu additions, however, were found to be detrimental on a general basis. Initial experiments with 5 wt. % Pb and Bi coatings demonstrated a strongly inhibitory effect on the high losses which normally occur as a consequence of reaction in the presence of excess Sn. This improved loss performance was not observed, however, when the experiments were repeated. The lack of reproducibility has been attributed to the overriding influence of Sn loading on the basis that a redistribution of the liquid metal occurring during the diffusion heat treatment may have resulted in a local condition of low Sn loading, which was responsible for the low losses of the first samples. However, this argument tends to be contradicted by the fact that the extent of Nb reaction shown by the metallographic data was normal for the excess Sn condition. Since the loss property as initially observed, particularly with respect to 5% Bi, reflected a very significant improvement, this aspect of the work warrants further review.
5. From the practical standpoint of producing Nb_3Sn tapes characterized by low ac losses, the overall results of the present study indicate that the liquid diffusion process should be operated under "Sn limited" reaction conditions. Cu must be excluded from the Sn coat, and since the alloys did not prove to be beneficial, the use of unalloyed Sn appears appropriate. This system of operation will, however, be characterized by disadvantages:

- a) convenient capability for the production of the thicker Nb₃Sn layers and high critical currents will be substantially reduced, and
- b) supplementary processing will be required for the restoration of solderability prior to lamination.

5.0 REMOVAL: DEVELOPMENT OF A PROCESS FOR SURFACE REFINEMENT

The work discussed in this section was conducted in parallel with the study of tin coating parameters (Section 4.0) through the initial two-thirds of the contract period; through the balance of the work schedule continuing development of the surface refining process system and its application to the production of illustrative samples was predominantly emphasized. As discussed in Section 2.0, the work was based on the methods and successful results of Bussiere and Suenaga^(11,12) with rod specimens.

Some limited exploration of mechanical polishing was performed with an abrasive drum machine, which had been used in another application for surface dressing Nb₃Sn tapes. A standard series of metallographic abrasives (silicon carbide papers, diamond compound and alumina polishing powders) was employed. Although a number of operating problems were encountered, some of the samples exhibited removal of the coarse surface layers when examined in metallographic sections. The tape appeared to tolerate the process without overt evidence of damage. The principal problem observed was that the face of the tape was incompletely polished, presumably because the wavy surface contour of the tape failed to conform to the drum surface. This approach was not continued, in part because of reservations about fragility and lack of flatness in the tape, but primarily because of the superior promise shown by the chemical method in concurrent experiments.

The initial experiments with chemical and electrochemical polishing utilized the bath employed by Bussiere: 4 parts HNO₃*, 1 part HF and 2 parts H₂O. Excessively high attack rates were observed in the etching of tape specimens at 25 C; in addition, black films (presumably niobium oxides) formed on the tape surfaces, an effect which was also observed in certain of Bussiere's experiments. A second bath featuring a reduced concentration of nitric acid (1.3 parts HNO₃, 1.0 part HF and 4.8 parts H₂O) eliminated the black surface film but again demonstrated excessively aggressive attack rates. Tape samples processed in either of these two baths exhibited complete removal of the Nb₃Sn layer after 30 sec. immersion without current.

*Formulations are described in terms of parts by volume of standard reagent acids: 70% HNO₃ and 52% HF.

Sisco and Epremian⁽¹⁵⁾ in their review of chemical and electrolytic polishing methods for niobium, listed a bath which utilized a methanol solvent base in order to repress ionization. The formulation for this etchant consisted of 3.4 parts HNO_3 , 1.0 part HF, 10 parts methanol and 6.9 g/l citric acid. Evaluation of this bath found substantially reduced attack rates, which were judged to be quite suitable for the controlled removal of the coarse structured Nb_3Sn surface layer. Indicated reaction time for the estimated polishing requirement was 48 sec. for the methanol bath, as compared to 12 sec. for the aqueous systems.

A subsequent series of exploratory experiments treated coupon samples by both the direct chemical (etching) and electrochemical (electropolishing) process systems. Two principal findings resulted:

1. If the tape was processed in the "as heat treated" condition, in which a surface layer of unreacted Sn is characteristically present, irregular dissolution effects were observed. Scattered traces of unreacted Sn remained on the surface of the tape (as observed in metallographic sections) in samples which were, on an average basis, well-etched. This presumably resulted from a relatively slower attack rate on the Sn than on the Nb_3Sn and/or a predominantly undercutting mechanism for Sn removal. Uniform polishing effects were easily obtained by using a preliminary etch in a nitric acid bath to strip the Sn.
2. The polishing effects achieved by electropolishing and by simple etching were not significantly different with respect to the rates of material removal and the surface regularity exhibited in metallographic sections. The lack of difference was presumably due to the facts that simple chemical dissolution is a high rate process, and that the currents used in the experiments were limited to about 0.4 amp/cm^2 .

Based on the generally favorable results shown by the coupon experiments, the chemical polishing of tape in a continuous process mode was undertaken. This work and the subsequent process development studies, which evolved as a consequence of initially successful results in reducing ac losses to an acceptable level, is the subject of this section of the report.

5.1 Experimental

The process for surface refinement and reduction of ac loss is a supplementary treatment of the Nb_3Sn tape after completion of the diffusion heat treatment step. The process sequence comprises three steps:

- Preliminary etching of the tape in a bath consisting of 1 part HNO_3 and 1 part H_2O . This step removes the surface layer of excess Sn remaining after Nb_3Sn formation and insures uniform material removal in the next operation.
- Primary etching of the tape to remove the surface layer of the Nb_3Sn , which gives rise to high ac losses. The etchant consists of 3.4 parts HNO_3 , 1.0 parts HF, 10 parts methanol and 6.9 g/l citric acid.
- Contacting the etched tape with liquid Sn at a temperature of about 1000 C. This step restores solderability for the subsequent fabrication of laminated conductor.

An equipment system for etching long lengths of tape by generally similar chemical procedures was available from other work done by IGC and was used without significant modification throughout the present program. This apparatus passed the tape through the etchant at a controlled rate and followed with a suitable rinse and dry sequence. The second rinse station of this system featured ultrasonic agitation, which served to dislodge adherent reaction residues from the surface of the etched tape. Two sequential passes through this system were used to accomplish the two steps of etching; this procedure was simpler than matching the two sets of residence requirements for the variable rate, short run experiments of current interest.

Two sizes of polyethylene etch tanks (3 liters and 16 liters) were employed from time-to-time; the larger volume of etchant was introduced primarily as a safeguard against a potential change of etch rate with solution usage. In either case, the immersion length for tape was 0.33 mm. Agitation of the etch bath was accomplished with the use of a magnetic stirrer. The Sn stripping treatment involved a residence time of 60 sec. in the HNO_3 bath at a temperature of 43-47 C. A bath temperature of 26-29 C was employed for the primary etchant; residence times were variable and are listed in the data.

The Sn coating operation was performed in a quartz reaction tube under an argon atmosphere; the melt was 100% Sn at a temperature of 1000 C.

The input superconductor for the experiments was produced by methods analogous to those described under Section 4.0; starting foils 21-24 μm thick and 19 mm wide were standard. Processing generally employed Sn-Cu alloy coatings.

AC losses were determined by the methods described under Section 3.0. The data reported for the first two experiments are the results of only one set of tests through the 200-1200 rms A/cm range of surface current density; the loss data shown for all later work are the averages of measurements performed on three samples at two levels of surface current density (500 and 1000 rms A/cm). Sample-to-sample deviation was not a significant factor in the results.

Metallographic data pertain to measurements on transverse cross sections with the use of a filar micrometer eyepiece.

5.2 Results

The results reported herein pertain entirely to a continuous mode tape etching process, which in principle is directly applicable to the production of long lengths of superconductor. In a few instances, coupon samples have been employed for special purposes (e.g., to determine dissolution kinetics, to establish and monitor process control data, and to provide correlation). When included, such data are so identified.

The initial experiment of this investigation treated a series of tape samples with varying residence in the etchant; tape speed was controlled to produce a series of residence times ranging from 0.5 to 1.5 min. Metallographic examination found that material removal had increased progressively with increasing residence time and that the coarse structured layer was apparently absent after 0.75 min. etching.

Loss measurements were subsequently made on this series of samples together with the "as heat treated" input material; these data were a part of that determined at the Brookhaven National Laboratory. The results, which are summarized in Table V-1 and displayed more extensively in Figure V-1, demonstrate the progressive

Table V-1

AC LOSS DATA FOR Nb₃Sn TAPES TREATED BY ETCHING
(Exp 75013.9)

Residence in Bath (Min.)	AC Loss ($\mu\text{W}/\text{cm}^2$)	
	500	1000
	<u>rms A/cm</u>	<u>rms A/cm</u>
Ni1	120	1020
0.50	80	830
0.75	35	510
1.00	21	400
1.25	12	330
1.50	10	260

INTERMAGNETICS

reduction of ac loss with the removal of surface layers from the Nb_3Sn tape and are analogous to those reported by Bussiere^(11,12) for the polishing of rod samples.

The loss data were correlated with the results of Nb_3Sn layer thickness measurements relative to the several steps of progressively deeper polishing. This study found that although the coarse structured surface layer observed in transverse metallographic sections had been eliminated by the 0.75 minute etch, additional loss improvement (35 to 10 $\mu\text{W}/\text{cm}^2$ at 500 rms A/cm) was achieved by the removal of 1-2 μm per side of apparently dense Nb_3Sn ; these data are shown in the graph of Figure V-2. This surprising observation indicates that presently observed microstructural features correlate imperfectly with loss behavior.

Figure V-3 shows the transverse cross section of a specimen which was etched for 1.5 min. Although the sample exhibits only dense Nb_3Sn as expected, the surface does not appear particularly flat nor smooth at the rather high magnification of the photograph.

Comparison of the results for the chemically polished samples with those for the Sn limited reactions with 100% Sn coatings shown in Table IV-1 indicates a significant behavioral difference. Although comparable loss levels can be observed at 500 rms A/cm for the two process systems, the corresponding losses at 1000 rms A/cm are substantially lower for the etched samples.

The next experiment of this study was initially conducted with the restricted objective of exploring the problems involved in restoring solderability to etched tapes. The input material was drawn from commercial stock, and had been produced with a knurled surface; the heat treated tape was etched for an arbitrarily selected time (1.1 min.). Experimental trials determined that tinning could be satisfactorily accomplished by passing etched tape through a 100% Sn bath at a temperature of 850-900 C and at a relatively slow speed (0.6 m/min.); the surface was not satisfactorily wetted when lower temperatures or higher tape velocities were employed. Metallographic examination found no evidence that retinning produced surface roughening or reforming of a coarse

INTERMAGNETICS

Fig. V-2: Etched Nb_3Sn Layer (7513.9).

The change in ac loss is shown as a function of the average two-side total thickness of residual Nb_3Sn after etching. The division of dense and coarse structure is based on the "as heat treated" specimen.

Figure V-3: Etched Nb₃Sn. The residence time in the etchant was 1.5 min. for this sample (7513.13). The ac loss was 10 $\mu\text{W}/\text{cm}^2$ at 500 rms A/cm (2350X).

structured layer. An approximately 10 m length of etched/retinned tape was laminated with copper foil, and a product exhibiting good physical quality was produced, thus demonstrating tentative feasibility for the retinning process.

Some of the samples from this experiment were subsequently examined with respect to loss properties in the "etched" and "retinned" conditions. The results, which are listed in Table V-2, not only show the absence of any degradation as a consequence of retinning, but also demonstrate a surprising reduction in losses for the "retinned" as compared to the "as etched" condition. Although a number of metallurgical reactions are potentially operative in the retin process, tin acting in the role of solvent to reduce surface roughness appeared to be the most probable explanation for the observed reduction of losses; the increasing effectiveness of loss improvement with increasing bath temperature is consistent with the expected kinetics of such a dissolution process. These results also demonstrated marked practicality for the processes under study, since the relatively simple supplementary treatment had improved the losses of commercial tape to the approximate level acceptable for power transmission application.

The basic processes of etching and retinning were subsequently integrated in an experiment which had the primary objective of showing reproducibility for the loss improvement demonstrated in the initial experiments. The work included measurement of the loss parameter at a series of process points: as heat treated, after the preliminary stripping of tin, and on a series of samples featuring a graded increase in the extent of etching. In addition, the losses were determined on samples of each of these variates after retinning (100% Sn, 1000 C, 0.3 m/min.). The results, which are listed in Table V-3, show two particularly interesting features:

1. The reduction of loss as a function of etching was quite similar to that demonstrated in the prior experiment, thus demonstrating process reproducibility.
2. The fact that retinning does not increase ac loss was confirmed: the low loss levels produced by several of the etching treatments were not significantly altered. Surprisingly, however,

Table V-2

AC LOSS DATA FOR Nb_3Sn TAPES
TREATED BY ETCHING & RETINNING

(Exp 75013C6)

Process Step or Treatment	AC Loss ($\mu\text{W}/\text{cm}^2$)	
	500 rms A/cm	1000 rms A/cm
Etched	32	400
Etched plus 800 C Retin	23	290
Etched plus 850 C Retin	15	240
Etched plus 900 C Retin	12	230

Table V-3

AC LOSS DATA FOR Nb₃Sn TAPES
TREATED BY ETCHING & RETINNING

(Exp 76001.1)

Process Step or Treatment	AC Loss ($\mu\text{W}/\text{cm}^2$)			
	500 rms A/cm		1000 rms A/cm	
	Initial Condition	After Retin	Initial Condition	After Retin
As Heat Treated	77	25	700	580
Sn Stripped	82	25	980	580
Etched: 0.50 min	22	14	540	310
Etched: 0.75 min	15	12	370	290
Etched: 1.00 min	14	15	330	250
Etched: 1.25 min	14	15	290	250
Etched: 1.50 min	11	13	240	220

the higher loss levels characterizing the unetched and mildly etched samples were substantially reduced by contact with the hot tin bath. As remarked above, tin acting in the role of solvent to reduce surface roughness appears the most probable explanation for this effect.

Short sample dc critical current (high field) was determined for two samples of this series: "as heat treated" and "etched 1.25 min. plus re-tin". The critical currents (1.27 cm width, 10 T field) were 490 A and 380 A respectively. The data show that this extent of etching removed a sufficient amount of the Nb_3Sn layer to significantly reduce critical current capability; yet, at the same time, this somewhat severely etched sample remains a very respectable superconductor. On the basis that critical currents in the power transmission environment will exceed the 10 T value by at least an order of magnitude, the expected rating of the etched sample would be in excess of 2990 A/cm.

The correlation between the chemical removal of the coarse structured surface layer of Nb_3Sn and the concurrent reduction of ac loss was also examined in this experiment. The pattern of behavior was analogous to that observed earlier. Although the 0.50 min. etch was enough to eliminate the coarse layer, further loss reduction characterized the more extensively etched variates. It might also be noted that the data of both experiments (Tables V-1 and V-3) failed to show a leveling-off in loss improvement and, consequently, imply that further benefits might derive from deeper etching.

The data of the preceding experiment demonstrated a reduction in losses from $77 \mu\text{W}/\text{cm}^2$ to $25 \mu\text{W}/\text{cm}^2$ (500 rms A/cm) caused by the contacting of "as heat treated" Nb_3Sn tape with liquid tin. This effect was further investigated in experiments which varied residence time from 0.1 to 6.4 min.; other conditions (100% Sn, 1000 C) were the same as in the prior work. The tapes used for these experiments exhibited losses of about $50 \mu\text{W}/\text{cm}^2$ (500 rms A/cm) in the heat treated condition. Exposure to liquid tin resulted in a progressive reduction of losses with residence increasing up to times of 0.4-0.8 min., at which a minimum of about $20 \mu\text{W}/\text{cm}^2$ was observed. Longer residence caused the losses to increase above the $20 \mu\text{W}/\text{cm}^2$ level, and after a residence of 6.4 min., the losses approximated those characterizing the "as heat treated" starting material.

No adequate explanation for these results has yet been deduced. The run order for the series of residence variates was randomized; this design feature of the experiment precludes the consideration of a potentially increasing concentration of Nb in the Sn bath as an explanation of the systematic response which was observed. Since the kinetics of the diffusion reaction are sufficiently rapid at these operating conditions to anticipate additional product formation at the longer residence times, it is relevant to question the appearance of additional Nb_3Sn which is characterized by a high ac loss. However, metallographic examination of the specimens found the unreacted Nb core to be essentially constant for all levels of bath residence, thus indicating that no substantial extent of new Nb_3Sn had actually formed; measurements of the Nb_3Sn layers supported this conclusion. Study of the metallographic cross sections also found no evidence suggesting the effects of dissolution attack or other surface roughening processes. The structural composition of the Nb_3Sn layer in terms of dense and nondense phases appeared generally similar throughout the sample group.

One series of samples was examined for critical current behavior based on dc short sample measurements at 10 T. An inverse correlation was found. With 0.8 minute residence in the tin bath, critical current increased progressively to a value about 25% greater than that of the "as heat treated" starting tape. Residence longer than 0.8 minute resulted in reduced values of the parameter: the critical current for the specimen treated for 6.4 minutes was 25% lower than the starting tape. The results of this experiment are shown in Table V-4.

Although the data are meager, the coincident occurrence of the quality optima for both the loss and current parameters is intriguing. It is also interesting to note that the run condition, which was selected for tinning effectiveness and utilized in the earlier experiments, featured a residence of 0.5 min., i.e., in the range of the presently indicated optimum. Although continuation of this investigation appeared warranted, the work was discontinued in order to proceed with the preparation of illustrative test specimens on the schedule required by the contract.

Table V-4

AC LOSS & CRITICAL CURRENT DATA
 FOR Nb_3Sn TAPES TREATED BY RETINNING
 (Exp 76003.5)

Residence In Sn Bath (Min)	AC Loss ($\mu\text{W}/\text{cm}^2$)		10 T Critical Current Surface Density (dc A/cm)
	500 rms A/cm	1000 rms A/cm	
Nil	48	600	330
0.1	23	470	-
0.2	24	490	-
0.4	21	470	370
0.8	17	460	410
1.6	23	470	360
3.2	30	430	280
6.4	47	520	250

5.3 Preparation of Sample Tapes

1) Specification

The requirements originally governing this group of samples were altered during the contract⁽¹⁶⁾. The new specification, which is shown in Appendix A, included the requirement that the Nb_3Sn layer be continuous around the edges of the tape. This product configuration substantially increased the complexity of sample processing: whereas the originally specified samples had been producible by a final slitting operation from a bulk length of tape, under the new requirement all samples were necessarily handled at finished width through most of the series of unit processes required. With the relatively fragile 6 mm wide tape which constituted the bulk of the specimens, this consideration constituted an extraordinary problem because tapes are customarily processed only at wider size and correspondingly greater strength. The new superconductor geometry introduced a further complexity in that more stringent requirements were imposed on the lamination process in order to adequately safeguard the fragile Nb_3Sn on the tape edges.

The additional work required for the preparation of specimens was accommodated by an appropriate modification of the work statement⁽³⁾, which deleted some of the tasks originally scheduled in this contract, particularly those addressed to pilot plant design and quality control planning.

2) Procedure & Results

Although all of the data reported on in the preceding sections of this report were not available when the process plan for the test specimens required a decision, the etch-retin system was clearly the method of choice based on its history of uniformly successful results in the process experiments. The work of producing the specimens involved four principal subdivisions:

- Preparation of the superconductor.
- Qualification testing to establish the control point for etch processing.

- Treatment of the required lengths of superconductor by the etch and re-tin process.
- Lamination of the superconductor with copper.

The superconductor was produced with the use of 22 μm thick Nb-1% Zr foil. The sequence of unit operations in the liquid diffusion process was arranged to form Nb_3Sn on the edge surfaces of the tape. The extent of reaction was regulated to retain a core of unreacted niobium about 12 μm thick, in order to assure safe handling of the narrow and relatively fragile tapes through the supplementary processes performed after heat treatment. Some concern was felt for this extent of restriction on Nb_3Sn formation, since it would in turn limit the extent of etching which could be performed for control of the loss parameter. Although short pieces of 6 mm wide conductor produced for BNL in concurrent work external to this contract had encountered substantial tape breakage in re-tinning, breakage was not a problem in the experimental studies even with relatively deeper reactions because of the substantially increased ruggedness of 19 mm wide tape.

In order to determine the control point for etch processing, short lengths of the tape were treated for varying residence times. System behavior with respect to the reduction of ac losses as a function of the extent of etching was found to be very similar to that defined by previously reported data.

Some examination of critical current behavior also appeared necessary; however, facilities are not presently available at this laboratory for the measurement of low field quench currents. Although no definitive correlation between high field critical current and transmission line quench current has thus far been established, it was thought that data for I_c at 10 T would be usefully instructive. As a guideline which is considered to be conservative, it was anticipated that quench current will exceed 10 T critical current by at least an order of magnitude. On this basis 250 A/cm (dc, 10T) appears as a quality marker relative to the present 2500 rms A/cm target specification for quench current.

Data obtained from the process qualification test is shown in Table V-5. The indicated decrease of critical current associated with improvement of the loss characteristic as a function of etch treatment, although not unexpected, posed a problem. The apparent remedy of forming a thicker layer of Nb_3Sn was not tenable for present circumstance, since a thicker starting foil would be required in order to sustain sufficient core thickness for a safe level of strength; time restrictions precluded procurement of the special foil. Consequently, a best accommodation of parameters was sought through control of the Nb_3Sn forming and etching processes, and the longer tapes required for specimen fabrication were produced. The results, which are listed in Table V-6, pertain to etched and retinned superconductor ready for lamination.

The 762 A and 762 B samples were 12.7 mm wide tapes about 7 m long; 762 E was a 6 mm tape about 120 m long. The results achieved in the longer length product run are compared with the process qualification data in Figure V-4. As indicated, some marginal improvement in loss was accomplished relative to the forecast properties, but the results appear closer to the limits of the target specification than is desirable. Although a more completely optimal relationship between the Nb_3Sn formation and removal processes could presumably have realized gains of perhaps 10-15%, these superconductors were regarded as both satisfactory and representative of the development status for the process innovation which has resulted from the work in this contract. Therefore, the required specimens were fabricated with these materials.

A substantial effort was devoted to improvement of an existing laboratory scale laminator, which appeared to offer the best approach for specimen fabrication. The tooling, which heats the strip and establishes registration in the laminate, together with associated machine elements that act to control the solder layer were redesigned. Experimental operations of some scope resulted in improved running procedure: e.g., a better effectiveness in the introduction of solder was accomplished by dip coating the superconductor with Sn - 3.5% Ag (375 C, argon atmosphere), and more satisfactory fluxing resulted from the use of a wiped film of palm oil.

Table V-5

AC LOSS & CRITICAL CURRENT DATA
FOR DELIVERABLE EXPERIMENTAL SPECIMENS

Qualification Test

Etch Residence (Min)	AC Loss ($\mu\text{W}/\text{cm}^2$)		10 T Critical Current Surface Density (dc A/cm)
	500 rms A/cm	1000 rms A/cm	
Nil (a)	48	590	460
Nil (b)	23	470	460
Nil (c)	26	490	500
0.50	20	280	260
0.75	17	270	190
1.00	15	260	110
1.25	14	300	60
1.50	10	330	30

Note: Data pertain to etched and retinned superconductor samples except:

- a) As Heat Treated
- b) As Heat Treated & Retin
- c) Sn Stripped & Retin

Table V-6

AC LOSS & CRITICAL CURRENT DATA
FOR DELIVERABLE EXPERIMENTAL SPECIMENS

Long Length Processing

Sample No.	Etch Residence (Min)	AC Loss ($\mu\text{W}/\text{cm}^2$)		10 T Critical Current Surface Density (dc A/cm)
		500 rms A/cm	1000 rms A/cm	
762 A	1.00	17	280	200
762 B	0.75	16	250	220
762 E	0.85	13	230	250

Note: Data pertain to etched and retinned superconductor

INTERMAGNETICS

Overall, this effort provided much improved experimental results with respect to minimizing misregistration, avoiding flux inclusion and maintaining thin, dense solder layers. Some difficulties were encountered, however, in the fabrication of specimens and served to illustrate that the problems of this demanding lamination are not completely resolved. This would especially apply in a production scale activity.

All three lengths of experimental superconductor were laminated. Satisfactory results were achieved with both the 762 A and 762 E samples, which on physical inspection were shown to be products of good quality; flat, well bonded and apparently free of serious defects. In the case of 762 B, however, several failures to achieve solder bonding occurred during lamination, and the sample was discarded.

The solder layer thickness in the 762 A and 762 E laminates was determined both by micrometer measurements of conductor thickness and by metallographic examination of transverse cross sections; average thickness was observed in the range of 0.30 to 0.40 mil. Misregistration in terms of superconductor exposure was examined by metallography, which showed an average exposure of about 1 mil for 762 E; 0.2 mil appeared characteristic in the cross sections of 762 A. Although the target specification for this contract allowed no exposure of the superconductor, the current BNL specifications (PTP Spec. No. 20 and 21) allow up to 1 mil. Nonetheless, a need for further improvement in the reliable control of registration is acknowledged.

The fabricated specimens were shipped to BNL for evaluation on May 11, 1976. Specimen 762 A consisted of 9 feet of 0.5 inch wide tape and satisfied the combined requirements established for critical current, ac losses and mechanical properties tests (see Appendix A). Specimen 762 E comprised 102 feet (2 pieces; 54 feet and 48 feet) of 6 mm wide tape and satisfied the requirement established for the coaxial test. The latter sample was 12 feet longer than the 90 feet specified: since the 6 mm tape was considered somewhat the better of the two conductors, the overage was submitted with the request that it be used for all the tests insofar as possible.

5.4 Summary

The work which has been reported on in this section has resulted in the development of a process for refining the surface topography of Nb_3Sn tapes produced by the liquid diffusion process so that ac losses are reduced to the present target specification for transmission cables. The process, which is a supplementary treatment applied to the Nb_3Sn after the usual heat treatment, consists of two principal steps:

- 1) etching to remove the surface layers of Nb_3Sn and to thereby reduce the ac losses to the required level of $10 \mu\text{W}/\text{cm}^2$ (500 rms A/cm), followed by
- 2) contacting the etched tape with liquid tin (1000 C) to restore solderability.

The method exhibited reliability and uniformly successful results in both the experiments of the process study and in the preparation of illustrative sample tapes.

Several noteworthy behavioral features which characterize the process have been observed in the course of the investigation:

- Although removal of the coarse structured surface layer of Nb_3Sn by etching produces the major extent of loss reduction (i.e., from the high level exhibited "as heat treated" to about $25 \mu\text{W}/\text{cm}^2$), further etching to remove some amount of apparently dense Nb_3Sn appears to be required for the critical improvement from 25 to $10 \mu\text{W}/\text{cm}^2$. The extent of etching performed in the experiments to date has failed to show a leveling off in loss improvement and consequently implies further benefits from deeper etching.
- The retin step also contributes to loss improvement in a way which is thought to relate to surface refinement accomplished by Sn acting in a solvent role. When "as heat treated" tapes were retinned without etching, losses dropped to a minimum of about $20 \mu\text{W}/\text{cm}^2$ as a function of increasing contact time; losses subsequently increased with longer bath residence. A coincident

maximum was observed in the critical current parameter. Loss improvement associated with retinning has been consistently demonstrated in the present series of experiments and is believed to have a high potential importance. Further work is required in order to elucidate the process mechanism and optimize its contribution.

- For the foil thickness on hand, production of the required experimental specimens necessitated restriction of Nb_3Sn formation in order to sustain adequate strength for the "in-process" handling of the narrow (6 mm) heat treated tapes. The work demonstrated a resultant problem: etching sufficient to achieve a fully satisfactory level of loss improvement caused an unacceptable reduction of critical current. Use of thicker than usual starting foils for preparation of the Nb_3Sn tape will accommodate both strength and etching requirements.

6.0 FUTURE RESEARCH & DEVELOPMENT

Of the two studies which have been reported on in detail in Sections 4.0 and 5.0, the removal process is recommended for further research and development, since it has been clearly demonstrated as a viable approach whereas the inhibition method did not demonstrate clear-cut results. The investigation of inhibition through control of tin coating parameters did delineate systematic behavioral traits which imposed a significant influence on loss characteristics; however, the system was characterized by only qualitative patterns of response and lacked quantitative reproducibility. Consequently, only general guidelines for manufacturing procedures addressed to a low loss product could be concluded.

The removal approach to the problem, however, had a markedly different outcome: a supplementary treatment process was developed and demonstrated to provide reliability and uniformly successful results in both the investigative experiments and in the preparation of sample tapes for evaluation tests by Brookhaven National Laboratory.

The need for a substantial extent of additional effort in the context of the removal approach is forecast. The primary technical problems are identified as follows:

- 1) Present information indicates that the production of transmission line conductor may require thicker Nb_3Sn layers, which would probably involve the use of thicker starting foils in the liquid diffusion process: i.e., thicknesses estimated to be in the range of 33-38 μm as compared to the 22-23 μm thickness which constitutes the upper level of ordinary present practice. The preparation of deliverable samples in the current work illustrated this problem, which is identified with the need for 6 mm tapes characterized by Nb_3Sn layers having continuity around the edges of the ribbon. A relatively thicker core of unreacted Nb must be sustained in order to provide sufficient strength in this comparatively fragile conductor for the required "in-process" handling after heat treatment. The standard thicknesses of starting foil

do not allow the heavier core in concurrent combination with Nb_3Sn layers having sufficient thickness to permit adequate etching for optimum loss improvement without excessively reducing critical current capability.

Adaptation of the liquid diffusion system for the processing of thick foils to produce high J_c Nb_3Sn is expected to be a substantial problem. Although feasibility for extrapolation of the present diffusion system into the regimen of thicker foils has been demonstrated, limited manufacturing experience with thick foil product has encountered problems in reliably sustaining the reaction for the increased extent of Nb_3Sn formation and in maintaining high critical current properties.

- 2) The current work has led to a very significant improvement in the loss properties of Nb_3Sn as a consequence of the retinning step which is included in the supplementary process system for the primary purpose of restoring solderability. Significant loss reduction (to the level of about $20 \mu\text{W}/\text{cm}^2$) has been accomplished by retinning "as heat treated" tapes without etching. This effect has been studied only superficially and is not well understood; further investigation is thus viewed as essential. If the loss improvement benefits associated with the retin process can be optimized, the requirement for etching may be minimized or possibly eliminated. In either event, significant mitigation of the thick foil problem would result. Significant cost reduction could accrue from such simplification of process requirements.
- 3) The kind of Nb_3Sn tape used, the formulation of the etchant and the use of 100% Sn in retinning represent initial choices in the planning of experiments. All have been retained because of the successful outcome of those experiments. Reconsideration of these choices, particularly with regard to mutual interaction, is required in order to achieve process optimization. For example, input Nb_3Sn tape produced under Sn-limited reaction

conditions to minimize the initial losses might contribute performance improvement and/or simplification. Selection of the etchant composition would presumably have a strong dependency on the specification of the input Nb_3Sn (e.g., composition of the tin coating).

- 4) As longer lengths of the product are prepared, process control must accommodate the changes of attack rate which can be expected to result from the accumulation of reaction products in the etch bath. Work must be directed towards characterizing such rate shifts and developing control methods which will either compensate for or stabilize against the effect.
- 5) Substantial improvements are required in the lamination process in order to satisfy the requirements of this demanding application. The problems relate to registration control, solder layer regulation and capability for reliable performance in manufacturing scale operations.
- 6) As discussed earlier in the report (Ref. 5.3-1), the tasks directed to pilot plant design and quality control planning were postponed as part of a necessary revision of the work plan for this contract. These tasks must be reactivated in the planning of subsequent work.
- 7) Certain problems have been identified in the measurement of losses (see Appendix B). These problems must be resolved, and the measurements procedure must be re-examined for use for quality assurance in production scale activity.
- 8) A more precise and comprehensive economic analysis must be performed, including the additional processing steps identified in the present effort.

APPENDIX A

SPECIFICATIONS FOR EXPERIMENTAL SPECIMENS SUBMITTED TO BNL FOR EVALUATION

Description of Samples⁽¹⁶⁾

1. Critical current and ac losses measurements - 3 pcs. 1/2 inch wide x 16 inches long.
2. Mechanical properties tests - 5 pcs. 1/2 inch wide x 12 inches long.
3. Coaxial tests - 30 pcs. 1/4 inch (6 mm) wide x 36 inches long.

Characteristics and Target Properties⁽¹⁷⁾

Losses

The ac losses are not to exceed $10\text{--}20 \mu\text{W}/\text{cm}^2$ at 500 rms A/cm and 4.2 K.

Current Capacity

The current capacity of the tape should be greater than 2500 rms A/cm at 4.2 K.

Bend Radius

The minimum bend radius is to be 0.3 inch to 0.4 inch.

Solder

Stabrite (95 Sn - 5 Ag) solder is to be used to join the tape components.

Nb₃Sn Layer

The Nb₃Sn should be continuous around the edges of the tape.

Stabilization

The tape is to be stabilized on both surfaces with 1 1/2 mil 150 R/R min copper. Registration between the Nb₃Sn substrate and copper clad should be such that on each edge the copper completely covers the substrate but does not extend more than 0.0025 inch beyond the edge of the substrate.

APPENDIX B

LOSS MEASUREMENTS

Operation of Wattmeter & Characterization of Accuracy

The use of the wattmeter in making the ac loss measurements required in this project was mentioned in Section 3.2. The following is a more detailed description of the wattmeter, its operation, and accuracy.

Wattmeter Technique

An ac superconducting solenoid is the source of the applied alternating magnetic field in which the losses are measured. A single layer probe coil is placed along the length of the tape sample, enclosing the sample within the coil. The sample of tape to be measured typically 5 cm long, is mounted to form part of a single turn around an epoxy fiberglass cylindrical bobbin which is placed in the central field of the solenoid. The probe coil, being at right angles to the alternating magnetic field, measures the electric field on the surface of the sample as a voltage. In terms of this experimental arrangement, the time-average Poynting vector loss per unit area may be expressed as

$$\frac{\bar{P}}{A} \left(\frac{\mu \text{ watts}}{\text{cm}^2} \right) = 10^6 \frac{f}{n\ell} \int_0^{1/f} \frac{10}{4\pi} H_z V_E dt$$

where H_z is the peak solenoid field in Oersteds, V_E the probe coil voltage in volts, l the effective probe coil length in centimeters, and n the number of turns in the probe coil.

In addition to the electric field probe coil, a second probe coil is placed in the alternating solenoid field as a source of signal to buck out the large, purely inductive voltage component in the electric field probe and as a measure of the magnetic field. The voltage of the magnetic field probe, which measures dH/dt , is integrated by the wattmeter to adjust the phase and give a voltage V_H proportional to H_z .

The V_E and V_H voltages are first amplified and then multiplied by the wattmeter. In addition to the gain settings G_E and G_H for the E and H amplification stages, and G_w for the multiplier stage, the meter has fixed internal gains A_E , A_H and A_w . The amplification stages give voltages

$$\tilde{V}_E = A_E G_E V_E$$

and
$$\tilde{V}_H = A_H G_H V_H.$$

The multiplier yields a voltage W proportional to the time average product

$$W = A_w G_w \tilde{V}_E \times \tilde{V}_H.$$

The probe voltage V_H is proportional to the ac field in the solenoid and may be expressed with inclusion of the coil constant, as

$$V_H = \frac{V_H}{I} \frac{I}{H} H$$

where I is the solenoid current.

Writing

$$f \int_0^{1/f} H_Z V_E dt = V_E \times H,$$

we have

$$\left(\frac{\bar{P}}{A}\right) \frac{\mu \text{ watts}}{\text{cm}^2} = \frac{\left(\frac{10}{4\pi}\right) 10^6}{(n\ell) (A_E A_H A_w)}$$

$$\times \frac{I}{V_H} \frac{W}{(G_E G_H G_w)}$$

In practice, the voltage-field relation for the H probe is calibrated in terms of its amplified voltage. In the previous expression we may substitute

$$\frac{V_H}{I} = \frac{1}{A_H G_H} \frac{\tilde{V}_H}{I}$$

giving the following working expression for use of the wattmeter:

$$\left(\frac{\bar{P}}{A}\right) \left(\frac{\mu \text{ watt}}{\text{cm}^2}\right) = \frac{\left(\frac{10}{4\pi}\right) 10^6}{(n\ell) (A_E A_w)} \frac{1}{\frac{1}{G_H} \frac{\tilde{V}}{I} \frac{I}{H}} \times \frac{W}{(G_H G_E G_w)}$$

The induced rms surface current in the tape in amps/cm is $J = \frac{10}{4\pi\sqrt{2}} H_p$, where H_p is the peak value of the field. The ac current in the superconducting solenoid is obtained from the shunt voltage, and the measured coil constant gives the peak field.

The experimental arrangement is shown in Figure B-1. The line voltage is used to drive the ac solenoid; an isolation transformer was found useful to eliminate line voltage drift and hence magnet current drift. The bank of capacitors limits the input current necessary to oscillate the magnet. The V_o channel input is from the E probe coil on the sample while the $M di/dt$ channel input is from the H probe coil. The scope permits observation of the degree to which the inductive signal in the E channel has been bucked out by the compensation provided from the H channel. The wattmeter output is measured on a digital voltmeter.

Wattmeter Operation and Accuracy

We have examined the wattmeter in detail, checking the performance of the multiplier section and measuring the phase shifts in the wattmeter itself. The multiplier non-linearities and the phase shifts in the wattmeter constituted the major sources of error in the readings.

We checked the multiplier by connecting the same 60 Hz signal to the X and Y inputs. The results we obtained are shown in Table B-1. The wattmeter closely follows the square law dependence as defined in the table, which is

$$V_{out} = 6.34 (V_{in})^2.$$

Inaccuracies at low powers are due to feedthrough and offsets in the multiplier.

We have measured these and found that at

$$x = 0 \quad Y = 8V \text{ rms}, \quad V_{out} = 0.029 V \text{ rms}$$

$$x = 8V \text{ rms} \quad Y = 0, \quad V_{out} = 0.068 V \text{ rms}$$

INTERMAGNETICS

AC LOSS FACILITY SCHEMATIC

FIGURE B-1

TABLE B-1

Wattmeter Multiplier Characteristics

Input (V_{in}) Volts rms	Output (V_{out}) Volts rms	$V_{out} = 6.34 (V_{in})^2$	% Error
0.035	0.079	0.007	1000
0.100	0.130	0.63	106
0.200	0.317	0.253	25
0.500	1.650	1.585	4
0.727	3.300	3.351	-1.5
0.859	4.750	4.678	+1.5
1.217	9.302+	9.387	-0.9
1.974	24.59+	24.71	+0.5
2.777	48.48+	48.65	+0.3
3.920	97.44+	97.44*	0.0

+ scaled from gain settings

* normalized at this point, i.e. the gain 6.34 is computed at this point

These spurious outputs are the same magnitude as the errors found at low power levels in Table B-1. If I_o is the input into one channel and V_o is input of the other channel, we estimate that the error due to offsets and feedthrough obeys the approximate equation

$$ERR = \frac{0.079}{6.34 \times V_o I_o}.$$

For example, if $V_o = 0.5V$ and $I_o = 0.1V$, the error can be as much as 25%. We find that multiplier errors should not exceed 2% at high powers ($V_{out} > 3.3$ volts) and should range from 4% to 25% at low powers ($0.317V < V_{out} < 1.65V$). In practice, we actually run with outputs greater than 1.21 volts rms and avoid most of the inaccuracies at low powers.

In doing these measurements, we discovered a 15% discrepancy in gain measurements from our previous measurements. This discrepancy was traced to the fact that the signal generator we were using, which has 600Ω output impedance, was being loaded by the multiplier. We have corrected the data using our present value for gain.

We also looked at the frequency dependence of the multiplier at 60, 120 and 240 Hz; we measured less than 10% variation in gain versus frequency.

To accurately measure the problems due to phase shifts in the wattmeter, we input the same 60 hz signal in V_o and $M \frac{di}{dt}$. The multiplier output should read exactly zero since the signal at $M \frac{di}{dt}$ is shifted by $\pi/2$ before it enters the multiplier. In practice, there is a small phase shift between the output V_o and I_o (the integrated $M \frac{di}{dt}$) output, which leads to a non-zero output of the wattmeter. We have measured this effect and from this we can infer what the inherent phase shifts are. The amplitudes of V_o output and I_o output were 11

and 7 volts respectively, so they can be represented by the following equations.

$$V_o = 11 \sin wt$$

$$w = 2\pi(60)$$

$$I_o = 7 \cos (wt + \Delta\phi)$$

$\Delta\phi$ is the sum of all phase shifts between V_o and I_o

The output of the wattmeter will be

$$\begin{aligned} V_{\text{wattmeter}} &= \text{Gain} \times \text{Time Average} (V_o(t) * I_o(t)) \\ &= 6.33 \times \frac{77}{2} \sin \Delta\phi \\ &= 243.7 \Delta\phi \text{ volts } \Delta\phi \ll 1 \end{aligned}$$

We measured 0.465 volts output from the wattmeter under these input conditions, which means $\Delta\phi = \frac{0.465}{243.7} = 0.0019$ radians. This result agrees with a computation of the phase shifts of the high pass and low pass networks in the wattmeter. The phase error of 0.0019 radians is most serious when the quadrature signal (the signal that is 90° away from the true power signal) is very large. To estimate this effect we break up the I_o signal into two components

$$I_o = I_p + I_Q$$

I_p = signal contributing power loss

I_Q = quadrature component
no power loss.

The wattmeter output will be to first order in $\Delta\phi$

$$V_{\text{out}} = (V_o I_p + V_o I_Q \Delta\phi) 6.33.$$

The phase error will contribute a power error whose percentage effect is

$$\text{Phase Error} = \frac{V_o I_Q \Delta\phi}{V_o I_p} = \frac{I_Q}{I_p} \Delta\phi.$$

Generally, $I_Q \ll I_p$ since the signal is bucked out in our calibration procedure

as much as possible. We found that errors of this nature should be less than $\Delta\phi$, or less than 0.2%.

A summary of our conclusions about the wattmeter accuracy is shown in Table B-2; the multiplier was the source of most of the errors.

Measurement Procedure and Accuracy

The procedure used at IGC is typical of loss measurements using the wattmeter method. The sample is secured inside the E coil of the probe; the E coil is taped to the probe and inserted into the bore of a superconducting solenoid. Field is applied by adjusting the output voltage of a variable transformer, and the current through the magnet is measured with a precision shunt. The outputs of the two coils are amplified and the two signals are multiplied together; an oscilloscope is used to monitor the input of the multiplier to be certain that the signal has not been clipped in the amplification stages. Gain settings of the wattmeter and its output are recorded.

In order to characterize the accuracy of this measurement a number of sources of potential error were examined. The accuracy of the wattmeter electronics was also checked and is discussed in another section.

Solenoid Field Profile - The solenoid used to generate the ac field was found to have a uniformity of better than 1% over a 3/4 inch axial distance, as shown in Figure B-2. The maximum sample size permitted by the probe is 0.75 inches and the maximum pickup coil width is 0.425 inches.

Eddy Currents in Probe Wires - The experiment was run without a sample in the E probe. Losses measured were primarily due to eddy current losses in the coils. Number 46 wire was initially considered for use in the E field coil but was

Figure B-2: Uniformity of Superconducting Solenoid @ 1600 gauss Central Field

TABLE B-2

SUMMARY OF WATTMETER ERRORS AND CORRECTION

Multiplier Linearity

High powers 2%

Low powers 4 to 25% due to offset and feedthrough

Multiplier frequency

dependence less than 1% at 60, 120, 240 Hz

Phase Errors 0.2% due to phase shifts before the multiplier

rejected in favor of number 50 wire, which exhibited much lower losses (Table B-3). Although the eddy current loss in the number 46 wire was small, it was proportional to σ and could contribute a significant error in the measurement of a very low loss sample.

Axial Movement of the Probe - There are two possible modes of error: the entire probe may be offset with respect to the center of the magnet, or the E probe may shift on the holder when the sample is installed. The former shifts both the E and the H coils, while the latter affects only the E coil. Changes with position reflect on the uniformity of the solenoid. Movement of the entire probe is a more severe test than movement of the E coil alone, since the E coil is in the region of best uniformity and the H coil is not. In both cases the changes are small and are of the order of the changes that have been seen in the repeatability experiment (Table B-4).

Probe and Sample Rotation - Rotation of the entire probe was initially found to produce a significant change in wattmeter output for low values of P (Table B-5). To determine whether the cause was direct pickup in the leads or improper radial centering of the probe in the magnet, the sample was moved to 90° and 180° with respect to the probe; the losses measured did not show any significant change with sample position. To reduce the direct pickup, the probe leads and high current leads were tightly twisted where possible, and the non-shielded length of the pickup leads was made shorter. The errors were reduced from those initially measured (Table B-6). Whether the remaining rotational variation is entirely pickup caused by non-optimum shielding or some other effect remains to be resolved.

TABLE B-3

E PROBE WIRE SIZE VS. EDDY CURRENT ERRORS

σ (amp/cm)	P ($\mu\text{W}/\text{cm}^2$) #46 Wire	P ($\mu\text{W}/\text{cm}^2$) #50 Wire
327	0.45	0.02
654	1.51	0.55
980	7.94	1.52
1307	11.1	2.47

TABLE B-5

POWER VS. ROTATION - BEFORE IMPROVEMENTS

Degrees	P ($\mu\text{W}/\text{cm}^2$) @ $\sigma = 500$	P ($\mu\text{W}/\text{cm}^2$) @ $\sigma = 1000$
0	6.8	307
60	6.7	306
120	6.2	304
180	5.8	303
240	6.1	304
300	6.6	306
360	6.9	307

$\sim 16\%$ @ $\sigma = 500$ $\sim 1.3\%$ @ $\sigma = 1000$

TABLE B-4

POWER VS. AXIAL MOVEMENT OF THE PROBE

σ	$P \text{ (}\mu\text{W/cm}^2\text{)}$ <u>normal position</u>	$P \text{ (}\mu\text{W/cm}^2\text{)}$ <u>sample up 0.1"</u>	$P \text{ (}\mu\text{W/cm}^2\text{)}$ Probe up 1/8" <u>Sample up 0.1"</u>
418	2.0	2.2	2.3
500	5.35	5.46	5.58
679	38.1	40.2	38.4
800	106	106	103
940	236	242	232
1000	311	310	304

E Probe Width - Most of the samples measured were 3/4 inch wide; thus, in order to avoid any possible edge effects, the E coil width was held to 0.425 inches. An experiment on a 1/2 inch sample using two different probe widths demonstrated the importance of keeping the probe width well below the sample width. The 1/2 inch sample was measured with higher losses at all current densities with the 0.425 inch probe than with the 0.3 inch probe normally used for 1/2 inch samples (Table B-7).

Repeatability - The reproducibility of a measurement on a sample was measured with the system in its final state. All of the possible errors, especially sample mounting, probe positioning and rotation would appear in the ability of the system to repeat a reading.

The sample used to check the repeatability was unclad and had low losses. Initial tests on the sample indicated losses of $\approx 5.4 \mu\text{W}/\text{cm}^2$ at 500 amp/cm. It was used as a reference during the time at which improvements were being made to the setup. The measured loss increased during this period and was attributed to the system changes. Losses of $\approx 9.5 \mu\text{W}/\text{cm}^2$ at 500 amp/cm were measured with the loss facility in its final state. Two weeks later the sample was found to have losses of $12.5 \mu\text{W}/\text{cm}^2$. No system changes had been made.

Experiments conducted on this sample to determine the origin of these increases showed an increase in losses every time the sample was measured. Thermal cycling without changing the sample mount continued to increase losses. Handling the sample between tests did not increase losses noticeably more than thermal cycling alone. A different piece of tape from the same length was measured. Losses compared well with the first set measured using the standard sample and the final setup; these data are summarized in Table B-8. On the basis of this test, it appears that the system is stable and capable of reproducibility within

TABLE B-6

POWER VS. ROTATION - AFTER IMPROVEMENTS

<u>Degrees</u>	<u>P ($\mu\text{W}/\text{cm}^2$) @ $\sigma = 500$</u>	<u>P ($\mu\text{W}/\text{cm}^2$) @ $\sigma = 1000$</u>
0	9.58	344.8
60	9.60	344.8
120	9.58	343.7
180	9.71	344.8
240	9.51	345.9
300	9.40	345.9
360	9.58	345.9

$\sim 3.2\%$ @ $\sigma = 500$ $\sim 0.6\%$ @ $\sigma = 1000$

TABLE B-7

E PROBE WIDTH VS. LOSS IN 1/2 INCH WIDE SAMPLE

<u>σ</u>	<u>P ($\mu\text{W}/\text{cm}^2$) with 0.425" probe</u>	<u>P ($\mu\text{W}/\text{cm}^2$) with 0.3" probe</u>
200	1.56	1.27
300	6.27	5.99
400	11.0	10.7
500	23.1	22.2
600	47.0	45.4
700	82.4	78.9
800	126	123
900	181	178
1000	250	243

TABLE B-8

REPEATABILITY AND SAMPLE DEGRADATION

<u>Sample</u>	<u>$P(\mu\text{w}/\text{cm}^2)$</u> <u>@ $\sigma = 500$</u>
Standard - as first measured	5.4
Standard - after final system modification	9.6
Standard - 2 weeks later	12.2
Standard - Thermal Cycle	13.1
Standard - Thermal Cycle	13.7
New sample from same length as Standard	9.9

the errors created by rotation and sample positioning. Reproducibility assessment was hindered by what appears to be deterioration of a particular sample caused by repeated testing.

This sample (759.6) was the 4.74% Pb/1.07 m/min. variate listed in Table IV-3. The listed loss $*8.0 \mu\text{m}/\text{cm}^2$) is a part of the data determined at BNL. Although the observed degradation is of some concern, it would not have constituted a variable in the loss measurements presented in the earlier sections of this report, since the listed data systematically pertain to virgin measurements.

Comparison with BNL - A sample of IGC tape which had been thoroughly evaluated was sent to BNL for comparative measurements. As shown in Figure B-3, IGC is in close agreement for higher loss values, but measures losses above BNL for low levels of loss.

Accuracy - The expected accuracy is based on all the errors that have been examined: in particular, rotation, positioning and the BNL comparison (see Section 3.0).

Future Research in Measurements

All of the errors identified and observed need to be eliminated wherever possible. The changes that occur with rotation are still not completely understood; twisting wires and better probe construction have helped, but have not eliminated the effect. The contribution of eddy currents in the walls of the aluminum dewar have never been determined, although the placement of the magnet 4 inches from the bottom of the dewar will hopefully keep this component small. Tests should be run using a stainless steel or a glass dewar.

INTERMAGNETICS

Tests should also be made to determine the cause of the apparent sample damage during repeated testing. Repeatability after thermal cycling, bending and time all need close attention.

In conclusion, measurement with the wattmeter is not completely clearcut. Work to understand and improve performance is necessary.

APPENDIX C

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