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Roger Goolsby
(M. S. Thesis)

September 1968
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THE CRITICAL TEMPERATURE OF $\text{Nb}_3\text{Sn}$ IN VARIOUS MICROSTRUCTURES

Roger Goolsby
(M.S. Thesis)
September 1968
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ABSTRACT

The effects of process variables on the microstructural distribution and critical temperature ($T_c$) of Nb₃Sn were studied. By utilizing two preparation techniques it was possible to prepare samples whose microstructures consisted of a Nb₃Sn film network surrounding a second phase of either niobium or NbC. The critical temperature of a sample with such a network was approximately the same as that for bulk Nb₃Sn.

One preparation technique consisted of sintering niobium, tin and carbon powders, while the other technique consisted of impregnating a porous niobium powder compact with liquid tin and reacting to form a Nb₃Sn film network at the niobium-tin interface. The critical temperatures of the samples were varied systematically by change of process variables, with $T_c$ values ranging from 15.9 to 17.8°K. For samples prepared by the sintering process, a linear relationship was observed between upper critical field and critical temperature. Efforts were made to refine the microstructure by obtaining a very thin ($< 1000 \text{ Å}$) Nb₃Sn film network, because it was anticipated that thin film superconducting effects would result if sufficiently thin films were obtained.
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1. INTRODUCTION

The discovery of the high-field properties of Nb₃Sn by Kunzler, et al.¹ in 1961 marked the beginning of a new era in the study and development of superconductors. Immediately investigators set about devising methods of fabricating wires and tapes of Nb₃Sn which could be wound as superconducting electromagnets. However, due to the brittleness of this compound, specialized fabrication techniques were required to accomplish this. Some of the more promising preparation techniques that have been developed are the powder core wire process¹,² vapor deposition process³, surface diffusion process⁴,⁵, and multi-layered wire technique⁶. It was discovered early that the method of preparation of Nb₃Sn greatly influenced its superconducting properties¹; so, investigators began to delve deeper into the factors influencing the critical temperature, current-carrying capacity, and upper critical field of Nb₃Sn.

The present investigation was initiated to study the critical temperature of Nb₃Sn prepared by a new technique. The method of preparation had been suggested and used by Olson⁷ and Chabanne⁸ in attempts to obtain improved current-carrying and critical-field properties of Nb₃Sn. These workers found that by hot-pressing the elemental powders niobium, tin, and carbon, a microstructure of NbC grains surrounded by a Nb₃Sn film was obtained. The sintered samples* prepared in this manner possessed very high values of upper critical field, Hc₂, and Chabanne felt that these high values were due to thin film superconducting effects. These effects, which occur when a superconducting film becomes very thin

* Throughout the remainder of this paper, samples prepared by direct hot-pressing of a niobium-tin-carbon powder mixture will be referred to as sintered samples.
(several hundred angstroms in thickness), result in significantly higher $H_c^2$ values than for a bulk superconductor. Attempts were made to refine the microstructure of the sintered samples, so that a very thin film network of $\text{Nb}_3\text{Sn}$ would be obtained, but these attempts were not successful.

When the present study was begun, it was thought that the current-carrying capacity and upper critical field of this system could be improved by refining the microstructure in two ways:

1. by obtaining a uniform microstructure with small NbC grain size; thereby creating more current-carrying paths of the superconductor, and

2. by reducing the thickness of the $\text{Nb}_3\text{Sn}$ film to dimensions thin enough to gain thin film superconducting effects. The microstructures of the sintered samples were controlled by varying the composition of the niobium, tin, carbon powder mixture and the sintering treatment given to the mixture. Eventually, a sample with an "optimum" microstructure of small-grained NbC surrounded by $\text{Nb}_3\text{Sn}$ was obtained, but the thickness of the $\text{Nb}_3\text{Sn}$ film could not be decreased smaller than several thousand angstroms. Also, this sample of "optimum" microstructure was obtained only after considerable effort.

Since it proved difficult to control the microstructure of samples prepared by the direct sintering process, another preparation technique was developed. This technique was designed so that the microstructures of the samples would be similar (superconducting film network) to that of the sintered samples. This method consisted of impregnating a very porous niobium compact with tin, and then heating the impregnated compact to the reaction temperature of $\text{Nb}_3\text{Sn}$. By controlling the time the compact was held at the reaction temperature, it was possible to obtain impregnated
samples* with microstructures consisting of niobium grains surrounded by a continuous network of tin, Nb₃Sn, and Nb₂Sn₃.

Although it is a well known fact that microstructure can have a dramatic effect on the superconducting properties of a compound like Nb₃Sn, relatively little work has been done in this area. The purpose of this study was to gain an understanding of the relationships between microstructure and critical temperature. Certain correlations between heat treatment, microstructure, and the critical temperature of Nb₃Sn have been observed.

* Throughout the remainder of this paper, samples prepared by the impregnation technique will be referred to as impregnated samples.
2. EXPERIMENTAL PROCEDURE AND RESULTS

2.1 Sample Preparation

2.1.1 Sintered Samples

The sintered samples were prepared by hot-pressing mixtures of niobium, tin, and carbon powders. The powders used throughout this research in the preparation of both sintered and impregnated samples were:

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Purity</th>
<th>Powder Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>niobium</td>
<td>Kawecki Chemical Company</td>
<td>99.9%</td>
<td>-325 mesh</td>
</tr>
<tr>
<td>tin</td>
<td>Cominco Electronic Materials</td>
<td>99.999%</td>
<td>-200 mesh</td>
</tr>
<tr>
<td>carbon</td>
<td>Union Carbide Corporation</td>
<td>&lt; 2 ppm</td>
<td>&lt;</td>
</tr>
</tbody>
</table>

Several different powder mixtures were used in sintered sample preparation, but the mixture of Nb\textsubscript{1} -Sn\textsubscript{0.56} -C\textsubscript{0.66} (atomic ratio) was used in making the majority of these samples.

Prior to the sintering treatment in the hot-press, the powder mixture was blended in a rotating jar. Once the mixture had been thoroughly blended, the mixture was placed in a double-acting graphite die. The die was then placed in the hot press, which was kept under a vacuum of approximately $5 \times 10^{-5}$ mm of mercury, and was pressed by means of a ram and sintered. The die was heated by means of a tantalum resistance filament which encircled the die. The geometry of the graphite die was designed so that samples obtained after hot-pressing would be rectangular parallelepipeds of dimensions 3 x 3 x 10 mm.

The sintered samples were processed according to one of two heat treatment schedules. These are shown schematically in Figure 1. Most samples were prepared by using a type A heat treatment. This involved
heating the graphite die to a high temperature $T_1$ (usually around 1900°C) for eight minutes, and then decreasing the temperature to temperature $T_2$ (approximately 1100°C) and sintering at this temperature for a somewhat longer period of time (either fifteen or sixty minutes). For samples prepared by heat treatment A, the die was always subjected to a ram pressure of approximately 8000 psi throughout the entire sintering process. Samples prepared by a type B heat treatment were heated to a much lower temperature $T_1$ (always less than 1100°C) than for heat treatment A. The die was held at this temperature for either fifteen or thirty minutes, and then heated to temperature $T_2$, which was much higher than the corresponding value of $T_2$ (1100°C) for heat treatment A, and held at this temperature for several minutes. In preparation of samples by heat treatment B, a ram pressure of either 1000 or 2000 psi was used.

The temperature of the graphite die was measured with a Leeds and Northrup optical pyrometer calibrated to read within $\pm 4°C$ on the low scale, $\pm 8°C$ on the high scale, and $\pm 20°C$ on the extra high scale. The low scale was used for measurements up to 1200°C, the high scale from 1200 to 1700°C, and the extra high scale above 1700°C. A horizontal surface of the die was used as a reference surface from which the pyrometer readings were made. The sightings were made through a quartz window in the hot press. The temperatures measured in this manner did not accurately reflect the true temperature of the sample on the inside of the die. This was confirmed by comparing optical readings on the surface of the die with readings from a thermocouple placed in the interior of the die. For example, when the die was heated to 1500°C as read by the thermocouple and held at this temperature for fifteen minutes, the temperature
as read optically off the die surface was 1420°C. However, this difference in temperature readings was negligible at 1000°C, and thus, the difference was significant at high temperatures and not at relatively low ones. All references to the high sintering temperatures are given solely for relative comparison between heat treatments.

Table I shows a summary of the exact heat treatments given to the sintered samples studied in this research. The samples are identified by a number such as S1840S. The first letter (S) identifies the sample as a sintered sample. The numbers following this letter identify the temperature $T_1$ at which the sample was heated. The last letter is only used in the identification of samples prepared by heat treatment A. It denotes the time the sample was held at temperature $T_2$ (1100°C). An "S" is used for fifteen minute anneals and an "L" is used for the sixty minute anneals.

2.1.2 Impregnated Samples

The impregnated samples were also prepared by using the hot-press; however, the preparation technique differed considerably from that of the sintered samples. Niobium powder was first hot-pressed at a ram pressure of 1000 psi and a temperature of 1400°C for thirty minutes. This resulted in a very porous, yet intimately connected, niobium compact. Tin powder was then placed in the space above the compact in the graphite die. The die was subsequently pressed at 1000 psi and heated to approximately 800°C for fifteen minutes, so that the tin melted and impregnated the porous niobium compact. The pressure which was applied to the die had to be kept relatively low, because higher pressures resulted in loss of tin from the entire die assembly. The temperature of the die
was then raised to approximately 1050°C for two to three minutes in order to react to form Nb₃Sn. The resulting sample was similar in dimensions to that obtained for the sintered samples.

A summary of the exact heat treatments for the impregnated samples is given in Table II. The impregnated samples have been identified by a designation such as IMP1. The letters (IMP) identify the sample as an impregnated sample. The number following these letters has no special significance.

2.2 Phase Identification

The different phases present in the microstructures of the samples were identified by utilizing these different techniques: (1) x-rays, (2) anodization, and (3) electron beam microprobe. X-ray analysis was made of samples in the "as pressed" condition using a Picker x-ray diffractometer.

The anodization method described by Picklesimer⁹ proved indispensable in delineating the many phases present in the samples. The samples were prepared for anodization by mounting in a suitable mounting powder such as Bakelite or Lucite, abrading on silicon carbide papers down to 600 grit, and polishing on a diamond abrasive wheel. Samples which were made from mixtures containing only niobium and tin powders required a special polishing technique, because these samples contained a microstructure which was predominately niobium and tin and could not be polished effectively on a diamond wheel. The technique consisted of a chemical-mechanical polish utilizing alumina in a solution of 20 ml
of 10\% NaOH solution, 10 ml of hydrogen peroxide, and 100 ml of distilled water.

Once the samples were polished, they were anodized at twenty-seven volts for six minutes in a solution of 120 ml absolute ethyl alcohol, 70 ml distilled water, 10 ml phosphoric acid, 20 ml lactic acid, 40 ml glycerine, and 1 g citric acid kept at room temperature. Anodizing conditions of voltage and time were standardized so that the individual phases present in the microstructure would consistently anodize as specific colors. For example, Nb$_3$Sn always anodized as a dark blue or violet color, while niobium anodized as a pale blue. The twenty-seven volt - six minute anodizing conditions were chosen so that direct comparison could be made with the results of Enstrom et al.\textsuperscript{10}, who also used these standard conditions. The phase/color relationships observed in the present study are shown in Table III, along with the relationships reported by Enstrom et al. The phase/color relationships reported by Enstrom et al conform fairly well with the relationships observed in this investigation. The anodized colors for the phases change from a basically blue color for niobium-rich compounds to a basically yellow color for tin-rich compounds, with compounds of intermediate compositions having brownish colors. This same general color trend has been reported by other workers\textsuperscript{11,12}, who used slightly different standard anodizing conditions.

The electron beam microprobe was used to identify and analyze the different phases delineated by anodization. The characteristic x-ray lines Nb-L\alpha and Sn-L\alpha were used to analyze the phases. The x-ray intensities measured with the microprobe were related to the phase compositions by use of a computer program developed by Frazer, Fitzgerald,
and Reid and later modified for use with computers at the Lawrence Radiation Laboratory. This program made corrections for dead time, instrument drift, background, and absorption. Correction for fluorescence was available in the computer program, but no fluorescence correction was made because the fluorescence yield factors for Nb-La and Sn-La in niobium-tin alloys are not known.

Electron beam microprobe analysis was conducted on several samples which had not been anodized. Later these same samples were anodized and analyzed with the microprobe again. The composition information determined for the anodized samples was not accurate enough to be used for quantitative purposes; however, the data for the samples in the polished condition was very reliable. Microprobe results for several of these samples are given in Table IV. The microprobe results on anodized samples were indispensable in the qualitative identification of phase vs. color.

Tables I and II give a summary of the phases identified in the samples and the different techniques used for the identification.

2.3 Critical Temperature Measurement

The superconducting transition temperature, $T_c$, of a sample was determined by observing the change in mutual inductance of two coaxial coils surrounding the sample. As a sample changed from the normal state to the superconducting state, as the temperature was varied, the mutual inductance of the coils changed, because of the exclusion of magnetic flux lines by the superconducting material. The coaxial coils were wound as primary and secondary coils, with the output of the secondary coil being amplified and plotted on a multi-channel recorder. Plotted
simultaneously on the recorder with the secondary coil output were resistance readings from a germanium resistance thermometer located near the sample. The germanium resistor was calibrated between 14 and 20°K using the vapor pressure of normal hydrogen. Both the coaxial coils and the germanium thermometer were contained within a massive copper block. Actually, the copper block contained six sets of coaxial coils, so that \( T_c \) measurements of six different samples could be made concurrently. A heater was also attached to the copper block, and the entire assembly was enclosed in a gas-tight copper cylinder.

First, the copper cylinder was filled at room temperature with helium gas to a pressure of 760 torr. The cylinder was then lowered into the liquid helium to cool the samples to a temperature well below the transition temperatures of the samples. Next, the cylinder was raised above the level of the liquid helium, and the temperature of the assembly was increased by means of the heater attached to the copper block. A temperature rise of approximately .15 to .20°K/min was maintained. A plot of the resistance of the germanium resistor and the output of the secondary coil for each sample was maintained throughout the temperature rise. As each sample changed from the superconducting state to the normal state, a significant change in the output of the secondary coil was observed. The critical temperature for each sample could readily be obtained from the resistance reading of the germanium resistor at that instant. Once the temperature of the assembly had been raised to approximately 20°K, which was well above the \( T_c \) for all the samples measured, the heater was turned off and the assembly was slowly cooled to a temperature below the \( T_c \) for the various samples. Again the temperature change was maintained at the same rate as for heating. This was accomplished
by varying the evaporation rate of the liquid helium past the cylinder. The evaporation rate was controlled by changing the power input in a resistor placed in the liquid helium. The heating-cooling cycle was usually performed twice during each test run, so that the $T_c$ for each sample was determined from four separate inductance changes. Critical temperature values were accurate to $0.1^\circ$K.

$T_c$ was defined as the temperature at which the secondary coil signal was the average of those signals for the completely normal and completely superconducting states of the sample. The width of the transition was defined as the temperature difference between 10 and 90% of the total secondary coil signal change. Critical temperature values for the sintered samples are shown in Table V, while the values for the impregnated samples are shown in Table VI.

2.4 Critical Field Measurement

A pulsed magnetic field test in liquid helium was used for the determination of the critical-current and critical-field properties of the samples. The pulsed magnetic field was applied perpendicular to the direction in which the simultaneously pulsed current was flowing in the sample. This technique is similar to that employed by previous workers $^7,^8$ at this laboratory. Jones $^4$ has given a complete discussion of both the experimental technique and the significance of the field results for all the samples studied in this investigation. Values of the upper critical field, $H_{c2}$, at $4.2^\circ$K are shown in Table V for the sintered samples and Table VI for the impregnated samples. These values of $H_{c2}$ are accurate to within $1\%$. 
3. DISCUSSION

3.1 Microstructure

3.1.1 General Discussion

The fact that processing has such a dramatic effect on the superconducting properties of Nb₃Sn makes it imperative that the relationships between microstructure and these superconducting properties be determined. With an understanding of how microstructure affects the superconducting properties of Nb₃Sn (likewise with other superconductors), superconducting properties can be optimized by controlling the microstructure. Basic to the control of microstructure of Nb₃Sn is the knowledge and understanding of the kinetics and phase equilibria of the niobium-tin system.

There have been several phase diagram determinations of the niobium-tin system¹⁰,¹¹,¹⁵-¹⁷. Although there still remain minor discrepancies among the published phase diagrams regarding exact values of composition and transformation temperatures of the phases, the diagram by Ellis and Wilhelm¹⁵ closely represents the consensus of these studies. This diagram, which is given in Figure 2, shows the existence of three intermetallic compounds in this system: Nb₃Sn, Nb₃Sn₂, and Nb₂Sn₃. One or more of these compounds was always present within the microstructures of the samples studied.

Both methods of sample preparation used in this investigation yielded samples whose microstructures contained several phases. Photomicrographs of the samples are shown in Figures 3 through 11. The identification of the individual phases required the use of several different techniques.

Samples were first tested for critical temperature transitions. The observance of a transition between 16 and 18°K indicated that Nb₃Sn was
probably present within the microstructure. X-ray diffraction analysis, which usually followed critical temperature tests, provided positive identification only of phases which were present in relatively large amounts. In most cases identification of phases which were present in small amounts could only be made through use of anodization and the electron beam microprobe.

3.1.2 Sintered Samples

The microstructures of the sintered samples generally consisted of NbC grains surrounded by a discontinuous film network of Nb$_3$Sn, Nb$_3$Sn$_2$, and tin. Photomicrographs of the sintered samples are shown in Figures 3 through 10. As can be seen from these figures, the microstructures of these samples were not at all homogeneous and often were very porous. With the exception of samples S1600L, S1050, and S500, the sintered samples had microstructures which included two contrasting regions. One region contained relatively thick grain boundary films and/or large pockets of tin. Figures 4(a), 4(b), 5(b) and 7(c) show this part of the microstructure for several samples. The other region consisted almost entirely of NbC, with very little of the Nb$_3$Sn film present. This region is clearly evident in the micrographs in Figures 5(a), 6(a) and 7(a). The reason for the difference in microstructure of samples S1600L, S1050, and S500 will be considered later, after a discussion of the effect of heat treatment on microstructure.

All of the sintered samples were prepared by heat treatments similar to one of the two types illustrated in Figure 1. All samples which were processed according to heat treatment A, with the exception of only S1600L, possessed microstructures as discussed in the preceding paragraph.
Samples Sl050 and S500 were prepared according to heat treatment B and their microstructures, which are shown in Figures 9 and 10, were noticeably different. The reason for the differences in the microstructures of these samples is directly related to the chemical reactions occurring during heat treatment.

Consider first the reactions which occur when a typical powder mixture is processed with a type A heat treatment. The mixture is routinely heated to a very high temperature, e.g. 1900°C, in a very short time, but the most important reactions, as far as determining the morphology of the microstructure, seem to occur during the first minutes of the heat treatment. First, the tin powders melt at about 230°C and, due to the surface tension, the liquid tin seems to separate into clumps. Next, the tin begins to react to form the intermetallic compounds of the niobium-tin system. However, once the temperature of the sample is above approximately 920°C, the only niobium-tin intermetallic compound that is stable is Nb₃Sn. At approximately 1400°C any remaining unreacted niobium present within the microstructure reacts with the carbon to form NbC. Thus, by the time the sample reaches temperature T₁ in the heat treatment, the morphology of the microstructure has probably already been determined. After the sample was held at temperature T₁ for eight minutes, the temperature was lowered to temperature T₂ (1100°C) and the sample was held at this temperature for either fifteen or sixty minutes. The purpose of this anneal was to improve the Tc of the Nb₃Sn which had been formed during the earlier portion of the heat treatment.

The microstructures of samples prepared by heat treatment A usually contained NbC, Nb₃Sn, Nb₅Sn₂, and tin. The Nb₅Sn₂ was probably formed
during the slow cooling of the samples from the 1100°C anneal to room temperature. One fact became very evident from studying the microstructures of samples prepared by heat treatment A. This was that once NbC had been formed, the NbC did not break down to form Nb₃Sn in the presence of tin at 1100°C (near the reaction temperature for Nb₃Sn). Such a large amount of carbon was maintained in the powder mixtures used for sample preparation, that once NbC had been formed, there was seldom any excess niobium available to react with the Nb₃Sn. Thus, reactions during the 1100°C anneal probably did not occur.

One correlation which could be made regarding the microstructures of samples prepared by heat treatment A was that generally for a higher sintering temperature $T_1$, there was less Nb₃Sn formed. A comparison of approximate percentage of Nb₃Sn vs sintering temperature $T_1$ is given in Table VII. The percentages were estimated by lineal analysis. The initial rate of temperature rise (from room temperature to temperature $T_1$), which was greater for higher values of $T_1$, seemed to be the important factor in determining to what extent Nb₃Sn was formed. If the rate was very rapid, then Nb₃Sn might not have been present at all in the microstructure of the subsequent sample. (This has been shown by the absence of high $T_c$ values for several samples which were prepared with very fast heating rates to $T_1$). With the rate somewhat less, Nb₃Sn was observed to form in an appreciable amount as a grain boundary film, with $T_c$ values approaching those of pure, stoichiometric Nb₃Sn. The drastic effect of the rate of temperature rise prompted a variation in the heat treatment schedule from that of a type A heat treatment to that of a type B heat treatment.
Samples S500 and S1050 are examples of the samples obtained by altering the sintering procedure to the type B heat treatment schedule. By changing the pressure and the temperature $T_1$ and the time at $T_1$, it was possible to obtain the uniform, small-grained microstructure that was desired, i.e. the microstructure of sample S1050. Even in this case, though, the Nb$_3$Sn network was not continuous and much excess tin was present. These two facts are readily apparent in Fig. 9. Efforts were made to improve the microstructure obtained in sample S1050 by changing the powder mixture ratio and the sintering schedule, but these efforts proved unsuccessful. The microstructure of sample S1050 represents the "optimum" microstructure prepared during this investigation. Sample S1050's superconducting properties, as evidenced in Table V, are very outstanding, but it is very clear from the micrographs that these are not the results of thin film properties. It is evident from the study of samples S1050 and S500 that the microstructures of samples prepared by the direct sintering process can be best controlled by a type B heat treatment. However, even using a type B heat treatment does not insure complete control of the microstructure. Since so much difficulty was encountered in controlling the microstructure of the sintered samples, it was decided that another method of preparation would be investigated, which might produce samples of similar microstructure that could be controlled more easily.

3.1.3 Impregnated Samples

The microstructure of impregnated samples was somewhat similar in morphology to the microstructure of sintered samples. The microstructure consisted primarily of niobium grains embedded in a sea of tin. At the
interface between the niobium and tin, reaction had occurred so that \( \text{Nb}_3\text{Sn} \) and \( \text{Nb}_2\text{Sn}_3 \) had formed. There was no evidence of a continuous thin film network of \( \text{Nb}_3\text{Sn} \) in the samples studied.

The impregnation preparation technique was developed because it was thought that samples with a thin, \( \text{Nb}_3\text{Sn} \) film network could be obtained. However, a major problem arose which inhibited the close control of sample microstructure. It was found that tin could not be made to flow into the porous niobium compact without reacting with the niobium. The tin would not flow into the compact until the temperature was approximately 800°C, because of the surface tension of the tin. Sample IMP1 was heated at 800°C to permit impregnation of the compact, and then the impregnated compact was immediately heated to 1050°C so that reaction to form \( \text{Nb}_3\text{Sn} \) would occur. Figure 11 shows the microstructure of this sample. In this figure niobium, \( \text{Nb}_3\text{Sn} \), \( \text{Nb}_2\text{Sn}_3 \), and tin are present. At first it was thought that the \( \text{Nb}_3\text{Sn} \) had formed at 1050°C and that the \( \text{Nb}_2\text{Sn}_3 \) had formed on cooling. However, another sample (IMP2) was prepared in an identical manner to that of IMP1 except for the short heating at 1050°C. The microstructure of this sample also contained additional phases other than niobium and tin. Sample IMP2 was tested for superconducting transitions and it was found that this sample contained a high \( T_c \) characteristic of \( \text{Nb}_3\text{Sn} \). Thus, it must be concluded that reaction occurred while tin was being heated for impregnation of the compact.

Attempts were made to impregnate the porous niobium compacts at lower temperatures, so that reaction between niobium and tin could be avoided, but these attempts were unsuccessful. A solution to this impregnation problem might be to add another element to the tin powder to
serve as a wetting agent. The tin would then flow much more easily at lower temperatures. Now, with the impregnated compact desired, the reaction to form \( \text{Nb}_3\text{Sn} \) in a thin film network could be easily controlled.

### 3.2 Critical Temperature

#### 3.2.1 General Discussion

The most distinctive property of a superconductive material is the near total loss of resistance at a critical temperature, \( T_c \). The value of \( T_c \) is characteristic of the material, and \( T_c \) values range from a few thousandths of a degree Kelvin to \( 20.5^\circ \text{K} \)\(^{18}\). The midpoint of the normal to superconducting transition, used to characterize \( T_c \), is \( 17.9^\circ \text{K} \) for \( \text{Nb}_3\text{Sn} \)\(^{19}\). The width of transition \( \Delta T_c \), may be of the order of a few millidegrees or may be as large as several degrees. Extensive work has been conducted in an effort to determine what factors influence \( T_c \) and \( \Delta T_c \).

The BCS theory, which was originally proposed in a series of publications by Bardeen, Cooper and Schrieffer\(^{20}\) in 1957, has been generally accepted as adequately describing the mechanism of superconductivity. This theory leads to the following fundamental equation describing \( T_c \):

\[
T_c = 1.14 \frac{\omega}{k_B} \exp \left( \frac{-1}{N(0)V} \right)
\]

where:
- \( k_B \) - Boltzmann's constant
- \( \omega \) - The phonon energy (proportional to the Debye Temperature, \( \theta \))
- \( N(0) \) - The density of states at the Fermi surface
- \( V \) - The net interaction energy between electrons

Unfortunately, it is still not possible to predict the \( T_c \) for a specific material with the above equation, because \( V \) is generally not known.
As a result scientists have had to rely heavily on experimental evidence and empirical considerations such as those developed by Matthias, De Sorbo and Roberts.

Livingston and Schadler have pointed out that for superconducting compounds like Nb$_3$Sn, the method of preparation is very important, because the critical temperature is sensitive to metallurgical variables. Both $T_c$ and $\Delta T_c$ have been observed to be influenced greatly by variations in composition of the superconducting compound. The departure from the ideal stoichiometric ratio of the compound has been shown to decrease $T_c$ and broaden the width of the transition for NbC, TaC, and Nb$_3$Sn. Impurities and lattice defects can also affect $T_c$. This is related to the manner in which the electron mean free path in the material is altered by the presence of the impurities or defects. Internal stresses, which could result during the preparation of a material, can also affect $T_c$. Inhomogeneity within the microstructure can be yet another important metallurgical factor which could alter $T_c$. Although a great deal has been learned about the relationship between microstructure and superconducting properties, there still remain many unanswered questions which must be investigated. In the present investigation several observations have been made regarding microstructural effects on critical temperature.

3.2.2 Sintered Samples

The most obvious correlation to be investigated in a study of this type was the relationship between heat treatment and critical temperature. From the data in Table V several observations were made concerning sintered samples prepared by heat treatment A. First of all, one general trend
that was observed was that, for higher values of the sintering temperature $T_1$ of a sample (all other variables in the heat treatment held constant), the critical temperature was lower. This has been illustrated in Table VIII where $T_c$ vs. sintering temperature $T_1$ data for samples S2030S, S1930S, S1840S, and S1730S are shown. All of the samples had identical heat treatments except for the value of temperature $T_1$. The second trend that was observed for samples prepared by heat treatment A concerned the effect of the time the sample was annealed at temperature $T_2$. As can be seen from Figure 12, samples with the sixty minute anneal at $T_2$ had better critical temperature values than samples prepared in an otherwise identical manner with only a fifteen minute anneal. The curves for samples S1950L and S1930S should be compared and samples S1730S and S1730L should be compared, since, except for the time at temperature $T_2$, all other heat treatment variables were the same. The effect of the longer anneal at $T_2$ seemed to be most pronounced for high values of sintering temperature $T_1$.

It has been shown$^{28}$ that Nb$_3$Sn, which has the Al5 crystal structure (shown in Figure 13), exists over a composition range of $\text{Nb}_x\text{Sn}_{1-x}$, where $x = 0.72$ to $0.80$. The effect of the heat treatment can be traced directly to the deviation from ideal stoichiometry of Nb$_3$Sn. Four sintered samples (S500, S1950L, S1730S, S1730L) were examined with the microprobe and the $T_c$ - chemical composition results are given in Table IV. These results are also shown in Figure 14. This figure shows that as the composition of the compound becomes richer in niobium, the critical temperature goes down. Bøchner et al.$^{29}$, Courtney et al.$^{30}$ and Reed et al.$^{28}$ found similar results; however, they found that at compositions of approximately 80%
niobium, the $T_c$ abruptly went to a very low value of approximately 5 to 6°K. Bachner et al. felt that this degradation in $T_c$ of Nb$_3$Sn was due to the volatilization of the tin atoms, with the subsequent motion of the vacancies to niobium atom sites in the A15 crystal structure. This would result in a discontinuity in the niobium chain, and Reed et al. had previously proposed that the continuity of these chains was the key to the high $T_c$ values in A15 compounds. The results of the present investigation certainly seem to be in complete agreement with the results of these workers.

The width of transition, $\Delta T_c$, is usually an indication of non-stoichiometry in the superconducting compound. From the data in Table IV, no clear correlation between deviation from stoichiometry and $\Delta T_c$ can be made; however, for the one sample (S500) that was very close to ideal stoichiometry, $\Delta T_c$ was very small. No positive correlations between heat treatment of the samples and their $\Delta T_c$ were observed; however, samples prepared at lower temperatures usually possessed smaller $\Delta T_c$ values.

In comparing samples which were prepared by heat treatment A with those prepared by heat treatment B, it can be seen that the latter possessed higher $T_c$ values than all of the samples prepared by heat treatment A, except for only sample S1600L. The formation of Nb$_3$Sn under conditions of the type B heat treatment seems to promote higher $T_c$ values.

One of the primary advantages of having a high $T_c$ in a high-field superconductor is that it means the superconductor will have a higher value of $H_{c2}$. This has been fully discussed by Berlincourt et al. and the primary relation between $H_{c2}$ and $T_c$ has been given as:

$$H_{c2} \propto \gamma \frac{T_c}{\gamma}$$

(2)
where:

- $H_{c2}$ - upper critical field
- $\rho_n$ - normal state resistivity
- $\gamma$ - electronic specific heat
- $T_c$ - critical temperature

Figure 15, which is a plot of $T_c$ vs. $H_{c2}$ for several sintered samples, exhibits a linear variation between $T_c$ and $H_{c2}$. This means that $\rho_n \gamma \approx$ constant for these samples. It would be anticipated that $\gamma$ would increase with increasing $T_c$, which is a maximum for stoichiometric Nb$_3$Sn. This would be expected because $\gamma$ is directly related to $N(0)$, the density of states at the Fermi surface, in equation (1). This would mean that $\rho_n$ should decrease with increasing $T_c$, since $\rho_n$ and $\gamma$ would vary proportionally to satisfy $\rho_n \gamma \approx$ constant. A lower $\rho_n$ for stoichiometric Nb$_3$Sn should be expected because of the more ordered state at stoichiometry.

One of the primary purposes of this investigation was to see if thin film effects of superconducting Nb$_3$Sn could be obtained. Although the $H_{c2}$ values are very high for the sintered samples, these values probably are not the result of thin film effects. The thickness of the film is not nearly thin enough in any sample to obtain these effects. Also, the Nb$_3$Sn films are very discontinuous, as can be seen in all micrographs of the sintered samples. One effect which might occur if thin films were present in the samples is the "proximity effect". This effect exists in a two-phase material when the proximity of one material affects the superconductivity of the other phase. This effect extends only a very short distance (i.e. the coherence length - typically 100 Å) from the interface, so that it is only significant for very
thin films. There was no evidence of a degradation of $T_c$ by the proximity effect in any of the samples studied.

3.2.3 Impregnated Samples

The $T_c$ values for samples prepared by the impregnation method are higher than those prepared by the direct sintering process. This is probably due to volatilization of the tin atoms and the subsequent vacancy migration to niobium atom sites in $\text{Nb}_3\text{Sn}$ formed in the sintered samples. The tin atoms would have more tendency to boil off in the sintered samples, because these samples were heated to much higher temperatures. The $T_c$ values of the impregnated samples were characteristic of bulk, stoichiometric $\text{Nb}_3\text{Sn}$. No thin film "proximity effect" on $T_c$ was observed.
4. SUMMARY AND CONCLUSIONS

By utilizing two preparation techniques (sintering process and impregnation process), it has been possible to prepare samples whose microstructures consisted of a Nb<sub>3</sub>Sn film network surrounding a fine-grained second phase (either niobium or NbC). The critical temperatures of these samples were characteristic of bulk Nb<sub>3</sub>Sn, and high-field properties typical of thin film superconductors were not observed.

With the sintering technique, it was possible to prepare a sample of very fine-grained NbC surrounded by a film of Nb<sub>3</sub>Sn. However, the Nb<sub>3</sub>Sn film was neither continuous nor thin enough to possess thin film superconducting effects. Several observations can be made regarding sintered samples and the technique by which these samples were prepared:

1. The distribution and thickness of the Nb<sub>3</sub>Sn film is determined primarily by the value of sintering temperature T₁.

2. The microstructure of these samples could best be controlled by a heat treatment involving the initial formation of Nb<sub>3</sub>Sn at a somewhat low temperature followed by a high temperature sintering to produce the NbC grains. However, with this type of processing there are some difficulties in reproducing the desired microstructure.

3. The critical temperature of Nb<sub>3</sub>Sn was found to decrease with increasing deviation from ideal stoichiometry. The degradation was probably due to the volatilization of tin atoms at high sintering temperatures and the subsequent migration of the vacancies to niobium atom positions.

4. A linear relationship between T<sub>c</sub> and H<sub>c2</sub> was observed. This would mean that the relation ρ<sub>n</sub>γ ≈ constant exists for
these samples.

(5) There was no evidence of a proximity effect on $T_c$ due to thin films.

The impregnation technique was developed after it proved very difficult to control microstructure using the sintering technique. The following comments can be made regarding this preparation technique and the samples prepared using it:

(1) Reaction occurred between niobium and tin during the impregnation of tin into the niobium compact.

(2) The impregnation would not take place at temperatures under 800°C, probably due to the surface tension of liquid tin. Impregnation of the niobium compact without reaction between tin and niobium might occur if wetting agents were added with tin, so as to lower the surface tension of the tin.

(3) Critical temperatures of impregnated samples were higher than those values for sintered samples, and these values for the impregnated samples were typical of stoichiometric $\text{Nb}_3\text{Sn}$.

This investigation has shown that by suitable alteration of the process variables, microstructure can be controlled so that a superconducting film network is obtained. The properties of a sample with such a network are roughly equivalent to that of the bulk superconductor. Two techniques have been developed which can be used to obtain microstructures of this morphology. However, the ultimate refinement of the thickness of the films remains an unsolved problem. The impregnation method (incorporated with a proper wetting agent) seems particularly promising, since reaction between niobium and tin can be controlled very easily. By further
refinement of processing techniques, i.e. reducing the film thickness by about one order of magnitude, a considerable enhancement of superconducting properties might be observed.
ACKNOWLEDGMENTS

The author would like to express his appreciation to Professors Victor F. Zackay and Earl R. Parker for their advice and encouragement throughout the course of this investigation. He also wishes to thank Masaki Suenaga for many helpful discussions and Dr. Eckhard Nembach for assistance with critical temperature measurements.

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REFERENCES


## Table I. Summary of Preparation Procedure and Phase Identification for Sintered Samples

<table>
<thead>
<tr>
<th>Sample*</th>
<th>$\theta_{T_1}$</th>
<th>$\theta_{T_2}$</th>
<th>NbC</th>
<th>Nb$_2$C</th>
<th>Nb</th>
<th>Nb$_3$Sn</th>
<th>Nb$_5$Sn$_2$</th>
<th>Sn</th>
<th>X-ray</th>
<th>Anodization</th>
<th>Electron</th>
<th>Transition</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>TL00L</td>
<td>200°C - 5 min</td>
<td>1100°C - 15 min</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>TL00L</td>
<td>1950°C - 5 min</td>
<td>1100°C - 60 min</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>TL00L</td>
<td>1930°C - 5 min</td>
<td>1100°C - 15 min</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>TL00L</td>
<td>1840°C - 5 min</td>
<td>1100°C - 15 min</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>TL00L</td>
<td>1730°C - 5 min</td>
<td>1100°C - 15 min</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>TL00L</td>
<td>1730°C - 5 min</td>
<td>1100°C - 60 min</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>TL00L</td>
<td>1600°C - 5 min</td>
<td>1100°C - 60 min</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>X</td>
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<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>TL00L</td>
<td>1050°C - 30 min</td>
<td>1000°C - 60 min</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>TL00L</td>
<td>500°C - 15 min</td>
<td>1500°C - 15 min</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

* Samples were prepared from an initial powder mixture of Nb$_1$ - Sn$_{0.56}$ - C$_{0.44}$ (atomic ratio).

** Figure 1 illustrates schematically the sintering treatment given the samples. All samples were pressed at a ram pressure of 8000 psi with the exception of samples S1050 (3000 psi) and S500 (2000 psi).

*** Identification of Nb$_2$C and Nb$_5$Sn$_2$ was not positive.
Table II. Summary of Preparation Procedure and Phase Identification for Impregnated Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_1 ) Temperature-Time</th>
<th>( T_2 ) Temperature-Time</th>
<th>( \text{Nb} )</th>
<th>( \text{Nb}_3\text{Sn} )</th>
<th>( \text{Nb}_2\text{Sn}_3 )</th>
<th>( \text{Sn} )</th>
<th>X-ray Diffraction</th>
<th>Anodization</th>
<th>Transition Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>2UP1</td>
<td>600°C - 15 min</td>
<td>1050°C - 2 min</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>2UP2</td>
<td>800°C - 15 min</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

* A run pressure of 1000 psi was applied during the entire impregnation procedure.

** Identification of \( \text{Nb}_2\text{Sn}_3 \) was not positive.
Table III. Color Scheme for Anodized Samples*

<table>
<thead>
<tr>
<th>Phase</th>
<th>Observed in Present Investigation</th>
<th>Reported by Enstrom et al. 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>light blue</td>
<td>blue</td>
</tr>
<tr>
<td>Nb3Sn</td>
<td>dark blue or violet</td>
<td>violet</td>
</tr>
<tr>
<td>Nb3Sn2</td>
<td>dark or reddish brown</td>
<td>red - purple</td>
</tr>
<tr>
<td>Nb2Sn3</td>
<td>orange - brown</td>
<td>orange - brown</td>
</tr>
<tr>
<td>Sn</td>
<td>light yellow</td>
<td>yellow</td>
</tr>
<tr>
<td>NbC</td>
<td>yellow</td>
<td></td>
</tr>
<tr>
<td>Nb2C</td>
<td>light brown</td>
<td></td>
</tr>
</tbody>
</table>

* Anodizing conditions: 27 volts, 6 minutes, Picklesimer's solution.

Table IV. Electron Beam Microprobe and Critical Temperature Results for Selected Sintered Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nb, Atomic %</th>
<th>Sn, Atomic %</th>
<th>Tc, °K</th>
<th>Δ Tc, °K</th>
</tr>
</thead>
<tbody>
<tr>
<td>S500</td>
<td>75.3</td>
<td>24.7</td>
<td>17.8</td>
<td>0.3</td>
</tr>
<tr>
<td>S1950L</td>
<td>75.7</td>
<td>24.3</td>
<td>17.3</td>
<td>1.6</td>
</tr>
<tr>
<td>S1730S</td>
<td>77.6</td>
<td>22.4</td>
<td>16.7</td>
<td>1.2</td>
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<tr>
<td>S1730L</td>
<td>78.4</td>
<td>21.6</td>
<td>16.4</td>
<td>2.0</td>
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</table>
### Table V. Superconducting Properties of Sintered Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_c$ ($^\circ K$)</th>
<th>$\Delta T_c$ ($^\circ K$)</th>
<th>$H_{c2}$ (kG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2030S</td>
<td>16.0</td>
<td>2.1</td>
<td>—</td>
</tr>
<tr>
<td>S1950L</td>
<td>17.3</td>
<td>1.6</td>
<td>234</td>
</tr>
<tr>
<td>S1930S</td>
<td>15.9</td>
<td>1.4</td>
<td>201</td>
</tr>
<tr>
<td>S1840S</td>
<td>16.3</td>
<td>3.0</td>
<td>—</td>
</tr>
<tr>
<td>S1730S</td>
<td>16.7</td>
<td>1.2</td>
<td>220</td>
</tr>
<tr>
<td>S1730L</td>
<td>16.4</td>
<td>2.0</td>
<td>215</td>
</tr>
<tr>
<td>S1600L</td>
<td>17.8</td>
<td>0.2</td>
<td>—</td>
</tr>
<tr>
<td>S1050</td>
<td>17.2</td>
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<td>228</td>
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<tr>
<td>S500</td>
<td>17.8</td>
<td>0.3</td>
<td>215</td>
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</table>

### Table VI. Superconducting Properties of Impregnated Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_c$ ($^\circ K$)</th>
<th>$\Delta T_c$ ($^\circ K$)</th>
<th>$H_{c2}$ (kG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMP1</td>
<td>17.6</td>
<td>0.3</td>
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</tr>
<tr>
<td>IMP2</td>
<td>17.6</td>
<td>0.2</td>
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Table VII. Estimated Percentages of Nb$_3$Sn in Sintered Samples Prepared by Heat Treatment A

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sintering Temperature $T_1$</th>
<th>% Nb$_3$Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2030S</td>
<td>2030°C</td>
<td>3%</td>
</tr>
<tr>
<td>S1950L</td>
<td>1950°C</td>
<td>8%</td>
</tr>
<tr>
<td>S1930S</td>
<td>1930°C</td>
<td>3%</td>
</tr>
<tr>
<td>S1730L</td>
<td>1730°C</td>
<td>12%</td>
</tr>
<tr>
<td>S1730S</td>
<td>1730°C</td>
<td>29%</td>
</tr>
<tr>
<td>S1600L</td>
<td>1600°C</td>
<td>19%</td>
</tr>
</tbody>
</table>

Table VIII. Comparison of Sintering Temperature $T_1$ and Critical Temperature for Selected Sintered Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sintering Temperature $T_1$ $(^\circ\text{C})$</th>
<th>$T_c$ $(^\circ\text{K})$</th>
<th>$\Delta T_c$ $(^\circ\text{K})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2030S</td>
<td>2030</td>
<td>16.0</td>
<td>2.1</td>
</tr>
<tr>
<td>S1930S</td>
<td>1930</td>
<td>15.9</td>
<td>1.4</td>
</tr>
<tr>
<td>S1840S</td>
<td>1840</td>
<td>16.3</td>
<td>3.0</td>
</tr>
<tr>
<td>S1730S</td>
<td>1730</td>
<td>16.7</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Fig. 1. Schematic heat treatment schedules for sintered samples.

(a) Typical Type A heat treatment temperature $T_1 > T_2$

(b) Typical Type B heat treatment temperature $T_1 < T_2$
Fig. 2. Constitution diagram for the niobium-tin system proposed by Ellis and Wilhelm.

XBL 688-5700
Fig. 3  Samples S2030S, Anodized  250x
Fig. 4(a). Sample S19501 Anodized 250X

Fig. 4(b). Sample S19501 Anodized 500X
1 - NbC, 4 - Nb₃Sn, 5 - Nb₅Sn₂, 7 - Sn.
Fig. 5(a). Sample S1930S Anodized 250x

Fig. 5(b). Sample S1930S Anodized 1000x

1 - NbC, 4 - Nb₃Sn, 5 - Nb₃Sn₂, 7 - Sn.
Fig. 6(a). Sample S17308 Anodized 250x

Fig. 6(b). Sample S17308 Anodized 1000x
1 - NbC, 2 - Nb₂C, 4 - Nb₂Sn.
Fig. 7(a). Sample SI7301 Anodized 100x

Fig. 7(b). Sample SI7301 Anodized 500x

1 - NbC, 2 - Nb₂C, 4 - Nb₃Sn, 5 - Nb₃Sn₂.
Fig. 7(c). Sample SL730L Anodized 1000x

1 - NbC, 2 - Nb₂C, 4 - Nb₃Sn, 5 - Nb₃Sn₂.
Fig. 8. Sample SL600L Anodized 250x.
Fig. 9(a). Sample S1050 Anodized 250×

Fig. 9(b). Sample S1050 Anodized 1000×

1 - NbC, 4 - Nb₃Sn, 7 - Sn.
Fig. 10(a). Sample S500 Anodized 250x

Fig. 10(b). Sample S500 Anodized 1000x

1 - NbC, 3 - Nb, 4 - Nb$_3$Sn, 5 - Nb$_2$Sn$_2$, 7 - Sn.
Fig. 11 Sample IMPI Anodized 500x
3 - Nb, 4 - Nb$_2$Sn, 6 - Nb$_2$Sn$_3$, 7 - Sn.
Fig. 12. Effect of anneal at sintering temperature $T_2$ on the superconducting-normal transition of sintered samples.
Fig. 13. $A_5$ ($\beta$-tungsten) crystal structure of $\text{Nb}_3\text{Sn}$
(from Woodard and Cody\textsuperscript{32}); $x = \text{nichelium, } o = \text{tin}.$
Fig. 14. Variation of critical temperature of Nb<sub>3</sub>Sn with deviation from stoichiometry for sintered samples.
Fig. 15. Variation of critical temperature with upper critical field for sintered samples.
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