Intermediate Phases in Superconducting Niobium-Tin Alloys

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(April 13, 1962)

In attempting to produce superconducting wire of the niobium sheath Nb₃Sn core type, it became apparent that results were generally unpredictable. Metallographic examination showed that such materials are heterogeneous and contain a number of intermediate phases. Detailed metallographic studies were made on diffusion zones in which tin had been allowed to react with porous niobium blocks, with fused niobium rod, and with niobium wires, and on a number of reacted powder mixtures.

The phases produced were identified by anodizing to characteristic colors and by micro-spot analysis, supplemented by some hot-stage microscope and thermal analysis tests. On the basis of these observations, a tentative revised diagram is offered to illustrate the types of reactions which occur in the system.

The presumably desired phase, Nb₃Sn, is found to lie between the more easily formed phases Nb₄Sn and Nb₂Sn₃, which are stable to temperatures well above the peritectoid decomposition of the Nb₃Sn. At lower temperatures the compound Nb₂Sn is formed. It is indicated that the high-temperature treatment to react niobium and tin should be followed either by very slow cooling or by an anneal in the 600 to 700 °C range to form Nb₃Sn.

1. Introduction

When the results from the initial investigations of the superconducting properties of the niobium-tin alloy “Nb₃Sn” were first disclosed, the Chemical Metallurgy Section was requested by the NBS Cryogenic Engineering Laboratory at Boulder, Colo., to produce some of this material. This was accomplished in a manner subsequently revealed in the initial report of Kunzler et al., [1], concerning the properties of this material. The outstanding performance of this NBS-produced wire was disclosed by Arp, Kropschot, and Wilson [2].

Although the original objective had been the attainment of an alloy, or rather an intermetallic compound of “β-Tungsten” structure, having the composition Nb₃Sn, the actual result of the processing of the material was shown by preliminary metallurgical investigations to be something quite different. The fact that the alloys prepared by any of several methods consisted of from four to six or seven different metallurgical constituents has been known and privately reported by this and other metallurgical laboratories.

This disclosure has profound significance in several areas. It must be recognized that we have not been dealing with a directly formed homogeneous material. Also, if it is correct to assume that only the Nb₃Sn phase has the desired superconducting properties, a minimum requirement is to achieve a continuity of this phase throughout the length of the conductor. A simplified “filament” or “thread” hypothesis, which tacitly assumes that when the resistivity is zero an infinitely small conducting path can carry an infinitely large current, is not sufficient to characterize a practical superconductor; it does not take into account the concept of “quality,” whereby one specimen can carry more current, or resist a higher magnetic field, than another specimen of the same size. Nevertheless, one can presume that any superconducting alloy wire does not necessarily need to be homogeneous, but does at least require one or more continuous paths of the desired superconducting constituent throughout the length of the conductor.

Initially, the superconductor, Nb₃Sn, was prepared by Matthias [3] who described its electrical properties. At a later date, Kunzler [1] arrived at several modes of Nb—Sn alloy preparations and treatments. However, the metallurgist realized, from previous experience with other systems, that treatment of niobium, with its extremely high melting point, and of tin, with its extremely low melting point, at temperatures far from the melting point of either could only result in extreme heterogeneity.

Experience in other laboratories had shown that, not infrequently, wires produced in the manner suggested by Kunzler failed to show the desired superconducting properties. As a consequence of all of these factors, it became evident that the physical metallurgy of this alloy formation would need to be carefully investigated if the process were to be adequately controlled. Previous to the interest in its superconducting properties, this alloy system had received but little metallurgical attention. A constitutional diagram of the binary Nb—Sn system was proposed by Savitskii et al. [4], figure 1. The only constituent shown, other than the terminal phases of the component metals, is the intermetallic compound Nb₃Sn, which is indicated as having been

1 Figures in brackets indicate the literature references at the end of this paper.
formed by a peritectic reaction near 2000 °C. These authors detected a reaction horizontal near 730 °C which they attribute to the presence of a monotectic between two tin-rich liquids.

The Savitskii diagram is certainly not compatible with the large number of phases which have been observed by microexamination of the alloy wires. Thus, the system must be further studied in order to identify positively the various phases and to establish the conditions for their formation.

2. Experimental Procedure

Rather than endeavoring to use the extremely fine wires prepared for superconducting experiments as subjects of metallurgical study, it was decided to use massive specimens. Diffusion studies were conducted using semi-sintered bars made from rather coarse-grained niobium powder. These were partially immersed in baths of molten tin for periods of from 4 to 400 hr at temperatures ranging from 700 to 1200 °C. Also, in each bath was placed a specimen of 1/4-in.-diam wrought electron-beam melted niobium.

The choice of the porous niobium bar was fortuitous because it provided two simultaneous experiments. First, by capillary action the molten tin was drawn up to fill all of the interstices in the niobium; thus the upper part of the bar represented conditions in the system where the amount of tin was limited. Second, the bottom of the specimen and the surfaces of both the porous bar and the wrought rod represented the tin-rich side of the system. In addition to these diffusion specimens, other specimens were prepared by compressing and sintering mixed powders and by fusion of the components. All of the resulting structures were heterogeneous.

The metallographic study of these materials was greatly facilitated by the use of anodic oxidation techniques suggested by Dr. M. L. Picklesimer of the ORNL. This procedure is an adaptation of a method first used for the study of zirconium hydrides [5]. Application of this technique imparts distinctive colors to the various microconstituents. These colors are uniform for each constituent for a single specimen and anodizing condition, but can be varied considerably by changes in the anodizing conditions. To prevent confusion in phase identification, the anodizing must be accurately controlled.

To eliminate polemic discussion between different observers examining the same or different microsections, it was decided to standardize the anodization of the present group of specimens so that niobium metal assumes a "Light Beryl Blue" coloration. To avoid use of multiple names for similar colors, it was agreed that the colors obtained under these conditions best match the colors in the Maerz and Paul Dictionary of Color [6] as follows:

- Nb: Light Beryl Blue Plate 33, E-1
- Nb₃Sn: Calamine Blue Plate 33, J-2
- NbSn: Orange Plate 33, D-11
- NbSn₂: Purple Aster Plate 43, J-7
- NbSn³: Buried Senna Plate 5, F-12
- Sn: Chrome Lemon Plate 9, K-2
- Impurity: Wisteria Plate 41, E-8

In order to verify the chemical compositions of the observed phases, numerous areas were subjected to microspot analysis on the NBS electron probe, a description of which is currently in preparation [7].

A number of the microstructures resulting from the reaction of powder mixtures of known composition are the subject of a concurrent quantitative metallographic analysis by means of a digital computer. These methods have recently been outlined by Moore, Wyman, and Joseph [8]. In this current work, color separation prints, showing each phase separately, are made from color photomicrographs, or alternately from color separation negatives made directly on the microscope. Each phase separation print is then scanned into the computer and analyzed for the total amount of that particular phase, the continuity or connectivity of the phase, and the mean free path for linear motion within the phase areas. Details of this effort will be described in another report. Some preliminary results of this quantitative metallographic study have been drawn upon in estimating the probable position of some of the phase boundaries indicated in this paper.

It may be of interest to note here that one such analysis was made on a color micrograph, furnished by Dr. Picklesimer, representing a selected "bad" section of a commercial Nb sheathed "Nb₃Sn" powder process wire. This section had been given a minimal reaction treatment prior to showing poor electrical properties, but other sections of the same

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**Figure 1. Constitution diagram of the niobium-tin system according to Savitskii et al. [4].**

![Figure 1](image_url)

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1 NBS spectrochemical analysis indicated the following impurity elements:
- Ag 0.001-0.011 δ
- Sn 0.001-0.011 δ
- Ag 0.001-0.01 δ
- Sn 0.001-0.01 δ
- Mn, Pb, Pt, Cu, Ti, Mo less than 0.001 δ.

2 NBS spectrochemical analysis indicated the following impurity elements:
- Al 0.001-0.01 δ
- Sn 0.001-0.01 δ
- Al 0.001-0.01 δ
- Sn 0.001-0.01 δ
- Ag 0.001-0.01 δ
- Sn 0.001-0.01 δ
- Ni, Pt.

3 Nb₃Sn phase.

4 NbSn phase.

5 NbSn₂ phase.

6 NbSn³ phase.

7 NbSn⁴ phase.

8 NbSn⁵ phase.
wire, given a more complete reaction, showed a normal superconducting quality. The "bad" area was found to contain 70 volume percent of the Nb₃Sn phase, of which at least 99 percent is interconnected by one or more circuitous paths, at least within the area of the micrograph. However, the mean free path within the Nb₃Sn phase, in a direction parallel to the axis of the wire, is only 0.027 mm. These results appear to indicate that the existence of a threadlike continuous path of convoluted shape is not in itself sufficient to guarantee useful superconducting properties; it would rather appear highly desirable to obtain wires so processed as to maximize the proportion of Nb₃Sn in the structure and produce a high level of simple linear connectivity between the particles of this phase.

3. Results

Due to the fact that these initial experiments were conducted for the purpose of simulating thermal treatments which had previously produced good superconductor wire, the subsequent observations must be considered from this viewpoint, that is, as but preliminary results.

The diffusion studies have shown that the niobium-rich side of the system quite readily forms the intermetallic compound Nb₃Sn, whereas the tin-rich side of the system forms the compound Nb₅Sn₃.

Between these two compounds, one finds the compounds Nb₅Sn and Nb₂Sn. Additionally, there is a eutectic between Nb₅Sn and the Sn-rich terminal phase occurring at about 215 °C and near 83 percent Sn.

3.1. Nature of the Nb₃Sn Phase

Preliminary studies of the melting of a specimen previously identified as consisting predominantly of Nb₃Sn revealed partial fusion at 1,950 ± 50 °C as determined with an optical pyrometer. Due to thermal gradients in the specimen, some portions were probably somewhat hotter, and in such an area subsequent microscopic examination revealed dendritic structure interspersed with small amounts of eutectic structure (fig. 5).

These observations lead to the conclusion that the compound Nb₃Sn melts congruently near 2,050 °C and that it forms a eutectic with the niobium terminal solid solution; the eutectic composition presumably is located near to that of the compound.

3.2. Electron-Probe Microanalyzer Measurements

The identification of the phases in the system was carried out primarily with the NBS electron-probe. After the specimens had been subjected to the anodic oxidation technique, the composition of each "color" was determined. The results are listed in table 1. Column 3 shows the actual probe results and their average, while column 4 shows the phase assigned to the color.

3.3. Metallographic Evidence for a Continuous Nb₃Sn Filament

In general, when a niobium block is immersed in molten tin and then slowly cooled from above 700 °C the surface becomes converted to Nb₃Sn, which gradually and uniformly penetrates the block. As the process continues, there is an irregular outward growth into the Sn. Upon cooling, the tin-rich areas of this zone transform to Nb₅Sn. Additionally, the tips of the fingerlike Nb₅Sn areas show the Nb₅Sn phases growing crystals into the molten tin. Also, discrete crystals of Nb₅Sn can be observed dispersed in the last areas to freeze.

If a continuous "filament" of Nb₃Sn is essential for superconductivity, conditions for its proper formation must be such that there are enough niobium particles in the mass to permit their surfaces to react, forming Nb₃Sn, and that these surface layers must form mutual contact in order to attain continuity throughout a wire length.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Color analyzed</th>
<th>Results (atomic percent Sn)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>34 hr at 1,200 °C+W.Q.</td>
<td>Calamine blue</td>
<td>22.3; 24.3; 22.8; 21.8; AV 20.6</td>
<td>Nb₃Sn</td>
</tr>
<tr>
<td>8 hr at 1,200 °C+S.C.</td>
<td>Eutectic blue</td>
<td>21.2; 21.9; AV 21.5</td>
<td>Nb₅Sn (7)</td>
</tr>
<tr>
<td>8 hr at 1,000 °C+S.C. (wire in tube)</td>
<td>Offshore needles in Sn (fig. 10)</td>
<td>22.6</td>
<td>Nb₃Sn</td>
</tr>
<tr>
<td>Reaction tube held at 800 °C+W.Q. Nominal 25% Sn.</td>
<td>Calamine blue (matrix)</td>
<td>17.0; 21.2; 24.4; 18.3; AV 20.3</td>
<td>Nb₃Sn</td>
</tr>
<tr>
<td>33 hr at 900 °C+S.C.</td>
<td>Orient</td>
<td>24.7; 28.5; 27.1; AV 26.5</td>
<td>Nb₃Sn</td>
</tr>
<tr>
<td>400 hr at 750 °C+S.C.</td>
<td>Orient</td>
<td>28.5</td>
<td>Nb₃Sn</td>
</tr>
<tr>
<td>200 hr at 700 °C+S.C. [Run (3)]</td>
<td>Orient</td>
<td>26.5</td>
<td>Nb₃Sn</td>
</tr>
<tr>
<td>200 hr at 700 °C+S.C. [Run (2)]</td>
<td>Orient</td>
<td>26.5</td>
<td>Nb₃Sn</td>
</tr>
<tr>
<td>Reaction tube held at 600 °C+S.C. Nominal 35% Sn.</td>
<td>Purple aster</td>
<td>25.1</td>
<td>Nb₃Sn</td>
</tr>
</tbody>
</table>

TABLE 1. Results obtained by means of electron-probe microanalysis

All percentages in this paper are atomic percentages.
The interiors of many of the porous bars were replete with examples of this action. However, the most striking example was one in which the periphery of a ½-in.-diam rod specimen became united with the flat surface of a porous bar during a 16 hr treatment at 1,200 °C, with subsequent furnace cooling. In this specimen the tangential interface was mainly \( \text{Nb}_3\text{Sn} \), with thin layers of underlying \( \text{Nb}_4\text{Sn} \) on each of the niobium bodies (fig. 6). Progressing away from the tangent area into the “V’s” showing remaining Sn, the layers on each niobium piece retained both the \( \text{Nb}_3\text{Sn} \) and \( \text{Nb}_4\text{Sn} \) and also revealed \( \text{Nb}_2\text{Sn}_3 \) needles forming on the \( \text{Nb}_3\text{Sn} \) and growing into the Sn.

### 3.4. Reaction of Niobium Wires in a Bath of Tin at 1,000 °C

In another set of experiments, small niobium wires were threaded into a ½-in.-I.D. niobium tube and the tube then filled with Sn. These specimens were treated for periods of 4, 8, 16, and 32 hr at 1,000 °C, the latter being water quenched, and the others furnace cooled.

The alloying in these specimens progressed in quite the same manner as that previously described. In addition, the \( \text{Nb}_3\text{Sn} \) “grew” out beyond the limits of the original niobium wire area and in turn developed the \( \text{Nb}_3\text{Sn} \) and \( \text{Nb}_2\text{Sn}_3 \) layers (fig. 7).

The 32-hr water quenched specimen revealed a completely new condition because from 43 wires originally within the tube, there remained but one very small speck of niobium surrounded by a few islands of \( \text{Nb}_3\text{Sn} \).

Rough measurements were made of the progress of the reaction layers in this series of treatments, the results being shown graphically in figure 2. Similar measurements of reaction depths on the interior of the niobium tube are shown in figure 3. The extent of the \( \text{Nb}_3\text{Sn} \) layer could not be measured due to the quite irregular nature of the surface. However, this phase was observed to be present in the 4-, 8-, and 16-hr specimens as a narrow zone of variable thickness lying between the overlying \( \text{Nb}_2\text{Sn}_3 \) crystals and the underlying \( \text{Nb}_3\text{Sn} \).

This wires-in-tube experiment points out the possibility of a new means of fabricating the Nb-Sn complex in such manner as to more completely insure a continuity of the \( \text{Nb}_3\text{Sn} \) phase throughout the entire length of the wire.

### 3.5. Diffusion Studies

The diffusion specimen which was water quenched after 32 hr at 1,200 °C (fig. 9) showed quite large amounts of \( \text{Nb}_3\text{Sn} \) in the reaction zones, together with infrequent crystal tips of \( \text{Nb}_2\text{Sn}_3 \), but no \( \text{Nb}_3\text{Sn} \) or \( \text{Nb}_2\text{Sn}_3 \). In contrast to this, the furnace cooled specimen had a reaction zone predominantly \( \text{Nb}_3\text{Sn} \) with frequent \( \text{Nb}_2\text{Sn}_3 \) tips (fig. 8).

In most of the slow-cooled specimens from the initial 700 to 1,200 °C diffusion series there was a distinct but very narrow band of precipitate in the Sn at a short distance from the Nb-Sn reaction surface. At the higher treatment temperatures, distinct needles were observed in this band. From their position, these needles were at first expected to be a high tin phase, but they were subsequently identified by color comparison in normal and in polarized light, and by electron probe analysis, as being composed of \( \text{Nb}_2\text{Sn}_3 \) (fig. 10).

Previous mention was made of the observation that the water-quenched wire-in-tube specimen
treated 32 hr at 1,000 °C revealed only a trace of niobium together with small particles of Nb₃Sn. No Nb₅Sn was in evidence. Similarly, in the diffusion series held at 1,000 °C, the 4-, 8-, and 16-hr slow-cooled specimens displayed islands of Nb₅Sn and a bit of Nb₃Sn in the Nb₅Sn bands (fig. 8).

After studying the microsections from the various diffusion experiments, the fact became evident that the Nb₅Sn phase can form quite readily from the Nb₃Sn phase on slow cooling. Quenched specimens retain only the Nb₃Sn.

As compared with the long diffusion times required to convert niobium particles or wires to Nb₃Sn, the conversion of Nb₅Sn to Nb₃Sn appears to proceed too rapidly to allow the diffusion of an additional 5 percent of tin into the converted areas. Such a difference might be expected if the Nb₃Sn phase dissolves excess tin, and thus approaches the Nb₅Sn composition.

Evidence of width for the Nb₃Sn phase was obtained by making electron-probe traverses across Nb₅Sn areas on a specimen quenched from 1,200 °C. The analytical values so obtained indicated a composition gradient of about 6 percent within the Nb₃Sn areas. This would place the tentative limits of the Nb₃Sn phase region at 17 and 23 percent at 1,200 °C, and confirm that only a small amount of additional tin is required for conversion to the Nb₅Sn phase.

### 3.6. Thermal Analysis

A specimen of nominal "Nb₃Sn" composition was subjected to thermal analysis (direct time versus temperature). This powder mixture had been pressed at 150 °C and 100,000 psi prior to loading into the furnace. The sample gave reproducible thermal arrests on three separate but continuous heating and cooling runs at 3 °C/min. Two thermal arrests on cooling occurred at 922 ± 5 °C and at 867 ± 5 °C and were easily detected from the temperature recording. The sample was later prepared for metallographic observation and it exhibited the Nb₃Sn, Nb₅Sn, Nb₃Sn, NbSn phases in an excess of Sn (figs. 11, 12).

Additional thermal analyses were run on pressed pellets of "Nb₅Sn" composition, but, in general, no strong arrests were noted. However, in one instance in which the sample was being held at a steady temperature near 1,150 °C, the furnace winding burned out and consequently the specimen cooled more quickly than the usual rate. During this cooling, the temperature record showed a definite arrest at 743 °C.

### Table 2. Results of thermal analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cooling rate</th>
<th>Arrest Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressed &quot;Nb₅Sn&quot; mixture</td>
<td>3 °C/min</td>
<td>917 °C, 829 °C</td>
</tr>
<tr>
<td>Compressed &quot;Nb₃Sn&quot; mixture</td>
<td>4 °C/min</td>
<td>927 °C</td>
</tr>
</tbody>
</table>

The thermal analysis data have been interpreted to assign the 863 °C temperature as the peritectic temperature of the Nb₅Sn compound and the 922 °C temperature as the liquidus for this composi-
reason for the observation that the reaction horizontals are difficult to detect by thermal analysis.

The original series of diffusion experiments revealed limited ranges of stability for Nb$_3$Sn, Nb$_5$Sn, and Nb$_2$Sn. The Nb$_3$Sn phase, appearing as a band at the reaction interface, is much more abundant at 700 °C than at higher temperatures. In the range from 750 to 900 °C this layer becomes thinner and discontinuous. In slowly cooled specimens from the higher temperatures, Nb$_3$Sn is usually found only at the tips of Nb$_5$Sn protuberances extending into the tin-rich liquid, or in pockets where tin has been trapped between niobium particles. These structures can be explained if Nb$_3$Sn decomposes thermally at some temperature below 900 °C, and if, at lower temperatures, it reacts with niobium or Nb$_5$Sn to yield Nb$_5$Sn and Nb$_2$Sn.

The Nb$_5$Sn phase, in turn, while generally present in significant amounts in the reaction layers of slowly cooled specimens, was essentially absent from all of the quenched specimens. Specimens which originally contained identified Nb$_3$Sn, including a special powder mixture prepared for this purpose, contained extensive areas of Nb$_5$Sn after heating to temperatures as high as 1,000 °C and quenching from 800 °C or higher. These observations appear to contain numerous contradictions and leave the true decomposition temperature of Nb$_5$Sn most uncertain.

3.9. Reacted Stoichiometric Mixtures of Niobium and Tin

In an effort to fix more firmly the position of the lines defining the interactions of Nb$_3$Sn, Nb$_5$Sn, Nb$_2$Sn, and Nb$_3$Sn, a series of specimens of accurately predetermined composition were prepared for quantitative metallographic measurement by the digital computer [8]. Mixtures of niobium and tin powders, covering the range from 10 to 60 percent tin, were hot pressed into pellets and then pressed into niobium tubes. The mixtures were reacted at 1,000 °C, cooled to low temperatures to establish a new equilibrium, and then quenched.

Preliminary examinations of these series may be summarized as follows:

Specimens water quenched from 1,000 °C contained only niobium, Nb$_3$Sn, and a quenched liquid, not Nb$_5$Sn crystals. The quenched liquid, by a preliminary material balance, appears to lie closer to 50 than to 60 percent Sn.

Specimens quenched from 800 °C were originally similar to the 1,000 °C specimens, with a very small amount of Nb$_5$Sn mixed in with the particles of high tin material. Critical examination of the specimen containing 60 percent tin, made some weeks after quenching, showed large amounts of Nb$_3$Sn, which apparently was stable at 800 °C. In the lower tin ranges, residual particles of Nb$_5$Sn or quenched liquid apparently had reacted with Nb$_5$Sn and niobium to form additional particles of Nb$_3$Sn.

Specimens quenched after 21 hr at 700 °C all showed considerable amounts of Nb$_3$Sn, which, however, had not yet replaced Nb$_5$Sn as the continuous phase. Thus these specimens were reacted below the decomposition temperature of Nb$_5$Sn, but as the reaction was proceeding slowly, it may be presumed that 700 °C is only slightly below this critical temperature.

Specimens slowly cooled after 18 hr at 600 °C showed both Nb$_3$Sn and Nb$_5$Sn in a matrix of Nb$_3$Sn. There were also a few particles of unreacted niobium. The identity of the Nb$_3$Sn phase was confirmed in this group of specimens by means of the electron-probe microanalyzer. These results are summarized in table 3.

<table>
<thead>
<tr>
<th>TABLE 3. Phases observed in reacted powder mixtures</th>
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<tr>
<td>Mixtures pressed, reacted at 1,000 °C, and finished by final reaction listed</td>
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</table>

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Nb</th>
<th>Nb$_3$Sn</th>
<th>Nb$_5$Sn</th>
<th>Nb$_3$Sn</th>
<th>Nb$_5$Sn</th>
<th>Quenched liquid</th>
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<tbody>
<tr>
<td>1,000</td>
<td>WQ</td>
<td>+</td>
<td>++</td>
<td>(n)</td>
<td>+</td>
<td>+</td>
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<tr>
<td>800</td>
<td></td>
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<td>740</td>
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<td>730</td>
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<td>700</td>
<td>QO</td>
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<th>Qd</th>
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<th>Orient</th>
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<tr>
<td>WQ</td>
<td>+</td>
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Thus, the decomposition temperature of Nb$_5$Sn lies between 800 and 1,000 °C, and must of necessity be of the peritectic form, while the decomposition of the desired Nb$_3$Sn phase lies below 800 °C and can be associated with earlier evidences of changes near 730 °C. The reaction observed in this temperature range is now seen to be due to the peritectoid decomposition of Nb$_5$Sn into Nb$_3$Sn and Nb$_2$Sn, and not to a monotectic at higher tin composition as originally presumed by Savitskii et al.

One additional observation on the pressed powder specimens is significant to the present discussion. After the specimens quenched from 800 °C had been stored for some weeks, all of the residual niobium particles could be seen to contain a barely resolvable Widmanstatten structure covering all of the central areas and extending to within a short distance (around 0.002 mm) from the surface (which is generally in contact with Nb$_5$Sn). This structure indicates that Savitskii's estimate of relatively extensive tin solubility in the terminal niobium phase should be accepted for the high-temperature range. However, the solubility limit must retreat at lower temperatures in the manner of a typical precipitation hardening solution.

3.10. Fractility in the Observed Intermetallic Phases

The hardness values for the three identifiable compounds have not as yet been determined. However, it was initially recognized by the early experimenters with Nb$_5$Sn that this compound was extremely brittle [1]. In fact, this brittleness is
highly detrimental to the processing of the wire into magnet windings because the slightest bending of a heat-treated wire will fracture the superconducting core. As a consequence, heat treatment must follow the coil forming.

Metallographic examination fully confirms this occurrence for it may be noted that areas of Nb₃Sn frequently abound with cracks. In addition to this, it was also noted that too much haste in specimen grinding resulted in the chipping out of Nb₃Sn areas.

The Nb₃Sn₃ phase exhibits a rather unusual friability. This phase is usually observed to form by outward growth into areas of the Sn-rich phase. In addition, individual crystals may be found in the Sn, adjacent to a reaction interface. The unusual feature to be noted is that both the "growing" crystals and the "free" crystals usually display severe cracking.

In contrast to these observations, the Nb₄Sn phase does not exhibit cracking, nor does it readily chip out during metallographic specimen preparation.

3.11. Impurity Inclusion in the Porous Niobium Bar

In addition to the phases so far identified, several of the diffusion couples have shown, in the porous niobium bar only, a streamerlike structure. These streamers appear as a wisteria color (fig. 9) when subjected to the anodic oxidation technique.

An attempt to determine the composition of these streamers was made by means of the electron-probe. The results showed that they contained no tin and about 60 to 70 percent Nb. Based on these data, it is felt that the streamers are extraneous to the binary system Nb-Sn. Furthermore, the wrought electron-beam melted niobium rod never showed these streamers or a phase of a color approximating wisteria. It is suggested that the probable identity of the streamers may be Nb₂N.

As the result of the investigations of the Nb-Sn binary system thus far conducted, the evidence clearly shows that the prior constitutional diagram is most incomplete. The tentative diagram shown in figure 4 is offered in its place as indicating the salient features of the system as shown by the investigations carried out to date.

4. Discussion

The present investigations have revealed several factors which are pertinent to any attempt to understand the physical metallurgy of the composite Nb—"Nb₃Sn" wires which have displayed such outstanding superconducting properties. Furthermore, the complete story of the physical metallurgy is essential to the process metallurgist in order that he may best fabricate this material, and to the physicist as a basis for further theoretical studies of superconductivity.
Nobium and tin react quite readily to form Nb₃Sn at temperatures far below the melting point of the compound. On the other hand, practical experience has shown that the direct formation of the compound Nb₃Sn either by diffusion of tin into solid niobium or by fusion of the components, seldom meets with material success.

In diffusion experiments near 800 °C, Nb₅Sn₃ appears to form quite readily in layers at the Nb-Sn—Sn interface, with crystals of Nb₅Sn₃ growing out into the tin and occasionally becoming detached. By contrast, the Nb₅Sn phase appears only as much thinner layers and is usually discontinuous.

This configuration can be expected when one realizes that the Nb₅Sn phase itself is not stable in this temperature range, and hence that the observed layer is found, on cooling, only in those areas where the composition is very close to 25 percent tin.

The extent of the areas which can transform directly to Nb₅Sn on cooling can be increased by control of the configuration of the niobium particles and of the degree to which the reaction with tin is allowed to progress. This control must prevent either excessive reaction with tin, which will produce reaction layers predominantly of Nb₅Sn₂, or excessive reaction of niobium, which will produce mainly Nb₅Sn. A diffusion reaction at or below 700 °C should avoid these undesirable reactions, but probably would require a very much longer reaction time than would be acceptable.

The problem of producing a homogeneous core of Nb₅Sn, either by fusion methods or by complete interaction of niobium and tin powders, involves first forming a mixture of Nb₅Sn and Nb₅Sn₂, followed by a peritectoid reaction between these products to form the Nb₅Sn.

The application of these phenomena to practical wire fabrication could take two distinct forms. If a continuous network of Nb₅Sn is sufficient to meet the requirements for superconductivity, niobium particles, preferably of elongated or fine niobium wires, may in effect be cemented together by a continuous film of Nb₅Sn. If the reaction is operated near 1,000 °C, the reaction time must be closely controlled in order to stop the reaction when material containing 25 percent Sn is most abundant. The amount of tin to be used in this case will be dictated in part by packing considerations, and might be well below 25 percent if much of the niobium is to remain unreacted.

If homogeneous Nb₅Sn must be produced, a mixture containing 25 percent tin may be reacted at or above 1,000 °C until the core is completely converted to Nb₅Sn and residual liquid. This mixture may then subsequently be annealed in the range 600 to 700 °C until the peritectoid conversion to Nb₅Sn is complete.

Probably the most significant practical result of this investigation will be to clarify the fact that the desired Nb₅Sn phase does not exist at the reaction temperatures normally employed in producing the superconducting complex. Thus, regardless of other details of fabrication, the attainment of a satisfactory superconducting structure will be directly associated with the rate of cooling from the reaction temperature; and, specifically, with the time that the material remains in the 600 to 700 °C range.

5. Conclusions

Current investigations of Nb—Sn superconducting materials have shown thus far that the Nb—Sn binary alloy system is much more complicated than had previously been assumed. A new constitutional diagram is proposed predicating from the results thus far obtained in the current investigations.

The intermetallic compound Nb₅Sn, which appears to be the desirable constituent for superconducting purposes, occurs between the compounds Nb₅Sn₃ and Nb₅Sn₂, which are stable to considerably higher temperatures. At lower temperatures, the system is further complicated by the formation of Nb₅Sn.

This seriously complicates the problem of attaining either a continuous body of homogeneous Nb₅Sn throughout a conductor, or of obtaining a controlled type of heterogeneous structure which will give a continuously interconnected network of the superconductor. The successful preparation of either type of structure will require critical control of the preparation and heat treatment of the material in order to overcome the inherent difficulty in forming the desired phase.

The previously described investigations were instigated and were conducted under the auspices of the Cryogenic Engineering Section of the NBS Boulder Laboratories, R. B. Scott, Chief. The advice and assistance rendered by Messrs. Arp, Corruccini, and Kropschot of this group is most deeply appreciated. Thanks are also extended to Messrs. C. A. Owens, W. J. Hall, and B. T. Sanderson of this laboratory for the preparation of specimens.

6. References

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*See ref. 6*
Figure 5. Eutectic type structure developed between some free niobium and Nb₅Sn after reheating a specimen of nominal 80% Nb—20% Sn composition quenched from 800, to about 1,850 °C. The matrix is Nb₅Sn. X1000.

Figure 6. Joint developed between the porous niobium bar (left) and the electron beam melted niobium rod (right). X100.
Figure 7. Cross section of a nominal 0.004-in. niobium wire heated for 8 hr at 1,000 °C in a bath of molten tin and furnace cooled.

The niobium shell is at the right. X500.

Figure 8. Interior of porous niobium bar after diffusion in a bath of molten tin for 16 hr at 1,000 °C followed by furnace cooling.

X200.
Figure 9. Interior of porous niobium bar after diffusion in a bath of molten tin for 32 hr at 1,200 °C followed by water quench. X200.

Figure 10. Exterior of niobium shell after diffusion in a bath of molten tin for 8 hr at 1,000 °C followed by furnace cooling.
The needles are Nb₄Sn. X1000.
Figure 11. Interior of thermal analysis specimen (nominal Nb<sub>2</sub>Sn<sub>3</sub> hot pressed pellet) after heating to 1050 °C at 3 °C/min followed by cooling to room temperature also at 3 °C/min. X200.

Figure 12. Interior of thermal analysis specimen (nominal Nb<sub>2</sub>Sn<sub>3</sub> hot pressed pellet) after heating to 1,050 °C at 3 °C/min followed by cooling to room temperature also at 3 °C/min. X1000.

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