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# Intermediate Phases in Superconducting Niobium-Tin Alloys

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In attempting to produce superconducting wire of the niobium sheath $Nb_3Sn$ 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 microspot 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, $Nb_3Sn$, is found to lie between the more easily formed phases $Nb_4Sn$ and $Nb_3Sn_2$, which are stable to temperatures well above the peritectoid decomposition of the $Nb_3Sn$. At lower temperatures the compound $Nb_3Sn$ 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 $Nb_3Sn$.

## 1. Introduction

When the results from the initial investigations of the superconducting properties of the niobium-tin alloy "$Nb_3Sn$" 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] [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 "$\beta$-Tungsten" structure, having the composition $Nb_3Sn$, 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 $Nb_3Sn$ 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 can 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, $Nb_3Sn$, 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 $Nb_3Sn$, which is indicated as having been

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[1] Figures in brackets indicate the literature references at the end of this paper.

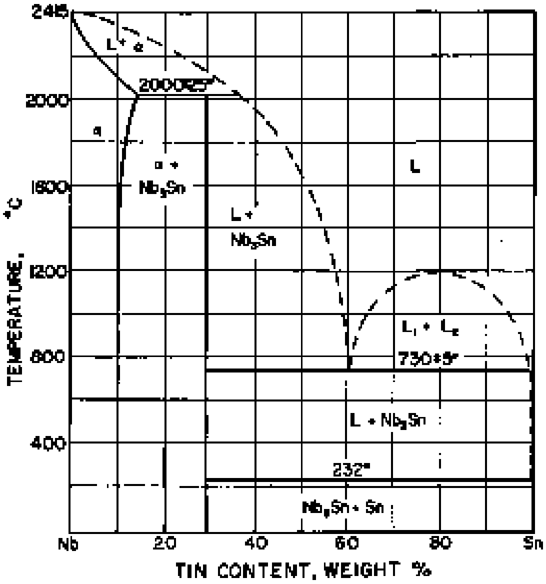

FIGURE 1. *Constitution diagram of the niobium-tin system according to Savitskii et al.,* [4].

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.[2] These were partially immersed in baths of molten tin for periods of from 4 to 400 hr at temperatures ranging from 700 to 1,200 °C. Also, in each bath was placed a specimen of 1/4-in.-diam wrought electron-beam melted niobium.[3]

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 |
| Nb$_4$Sn | Calamine Blue | Plate 33, J–2 |
| Nb$_3$Sn | Orient | Plate 36, D–11 |
| Nb$_2$Sn | Purple Aster | Plate 43, J–7 |
| Nb$_2$Sn$_3$ | Burnt Sienna | Plate 5, F–12 |
| Sn | Chrome Lemon | Plate 9, K–2 |
| Impurity | Wistaria | 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 "Nb$_3$Sn" 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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[2] NBS spectrochemical analysis indicated the following impurity elements: 0.01–0.1% Fe, Si; 0.001–0.01% Al, Ca, Cr, Cu, Mg, Ni; less than 0.001% Ag, B, Mn, Pb, Pt, Ta, Ti.

[3] NBS spectrochemical analysis indicated the following impurity elements: 0.01–0.1% none; 0.001–0.01% Cr, Fe, Mg, Si; less than 0.001% Ag, B, Ca, Cu, Ni, Pt.

wire, given a more complete reaction, showed a normal superconducting quality. The "bad" area was found to contain 70 volume percent of the $Nb_3Sn$ 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 $Nb_3Sn$ 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 $Nb_3Sn$ 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 $Nb_3Sn$, whereas the tin-rich side of the system forms the compound $Nb_2Sn_3$. Between these two compounds, one finds the compounds $Nb_3Sn$ and $Nb_2Sn$. Additionally, there is a eutectic between $Nb_2Sn_3$ and the Sn-rich terminal phase occuring at about 215 °C and near 83 percent[4] Sn.

### 3.1. Nature of the $Nb_3Sn$ Phase

Preliminary studies of the melting of a specimen previously identified as consisting predominantly of $Nb_3Sn$ revealed partial fusion at $1,950 \pm 50$ °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 $Nb_3Sn$ 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 $Nb_3Sn$ 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 $Nb_3Sn$, 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 $Nb_3Sn$. Additionally, the tips of the fingerlike $Nb_3Sn$ areas show the $Nb_2Sn_3$ phases growing crystals into the molten tin. Also, discrete crystals of $Nb_2Sn_3$ can be observed dispersed in the last areas to freeze.

If a continuous "filament" of $Nb_3Sn$ 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 $Nb_3Sn$, and that these surface layers must form mutual contact in order to attain continuity throughout a wire length.

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[4] All percentages in this paper are atomic percentages.

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

| Treatment | Color analyzed | Results (atomic percent Sn) | Phase |
|---|---|---|---|
| 34 hr at 1,200 °C+W.Q. | Calamine blue<br>Impurity | 22.3; 21.5; 19.4; 21.0→Av 21.0<br>0 (60-70 Atomic percent Nb) | $Nb_3Sn$<br>$Nb_3N$ (?) |
| 8 hr at 1,200 °C+S.C. | Eutectic in Sn | 83.6; 83.3→Av 83.4 | |
| 8 hr at 1,000 °C+S.C. (wire in tube) | Offshore needles in Sn (fig. 10) | 22.6 | $Nb_3Sn$ |
| Reaction tube held at 800 °C+W.Q. Nominal 20% Sn. | Calamine blue (matrix) | 17.0; 23.2; 24.4; 18.5;→Av 20.8 | $Nb_3Sn$ |
| 32 hr at 900 °C+S.C. | Orient<br>Burnt sienna | 24.7; 28.5; 27.1→Av 26.8<br>58.7 | $Nb_3Sn$<br>$Nb_2Sn_3$ |
| 400 hr at 750 °C+S.C. | Orient<br>Burnt sienna | 26.5<br>69.0 | $Nb_3Sn$<br>$Nb_2Sn_3$ |
| 200 hr at 700 °C+S.C. [Run (1)] | Burnt sienna | 60.4; 61.6; 61.0; 62.1; 59.7→Av 61.0 | $Nb_2Sn_3$ |
| 200 hr at 700 °C+S.C. [Run (2)] | Burnt sienna | 59.3; 59.3; 60.5; 58.0; 60.5→Av 59.3 | $Nb_2Sn_3$ |
| Reaction tube held at 600 °C+S.C. Nominal 30% Sn. | Purple aster<br>Calamine blue (matrix)<br>Orient | 29.9; 29.3; 29.2; 30.2; 32.3→Av 30.2<br>21.8; 21.1; 18.6; 19.5→Av 20.6<br>25.1 | $Nb_2Sn$<br>$Nb_3Sn$<br>$Nb_3Sn$ |

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 ¼-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 $Nb_3Sn$, with thin layers of underlying $Nb_4Sn$ 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 $Nb_4Sn$ and $Nb_3Sn$ and also revealed $Nb_2Sn_3$ needles forming on the $Nb_3Sn$ and growing into the Sn.

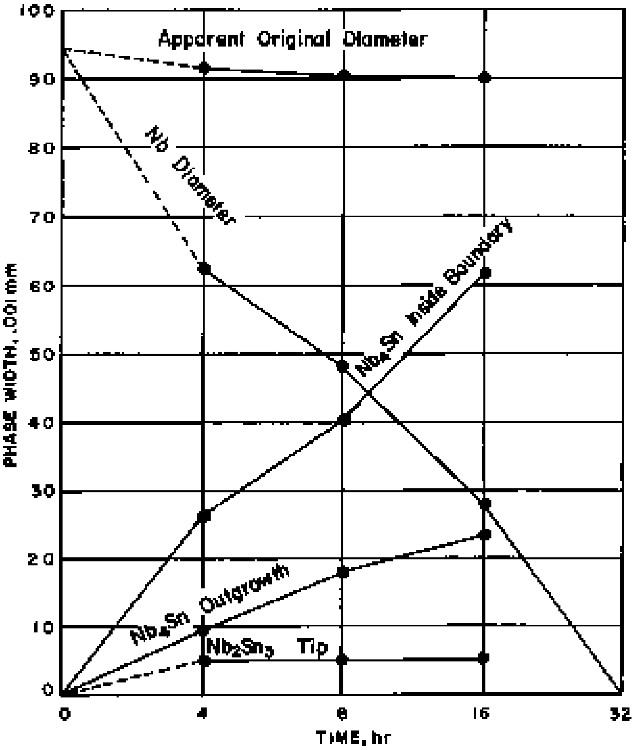

Figure 2. *Growth of reaction layers on 0.004-in. niobium wires versus time in molten tin at 1,000 °C followed by furnace cooling.*

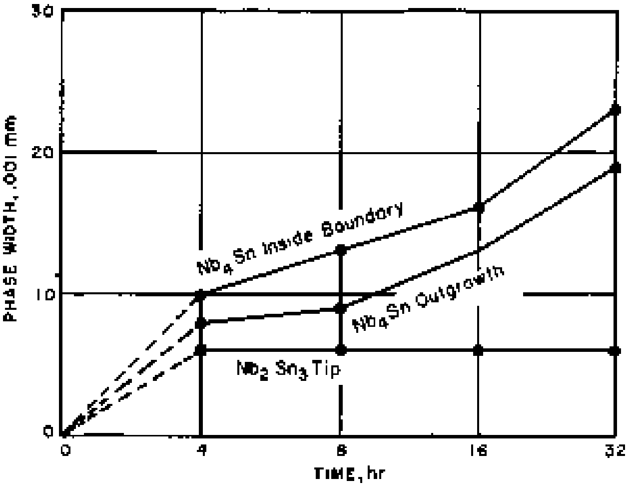

Figure 3. *Reaction depths on the interior of the niobium shell versus time in molten tin at 1,000 °C followed by furnace cooling.*

## 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 ⅛-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 $Nb_4Sn$ "grew" out beyond the limits of the original niobium wire area and in turn developed the $Nb_3Sn$ and $Nb_2Sn_3$ 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 $Nb_4Sn$.

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 $Nb_3Sn$ 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 $Nb_2Sn_3$ crystals and the underlying $Nb_4Sn$.

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 $Nb_3Sn$ 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 $Nb_4Sn$ in the reaction zones, together with infrequent crystal tips of $Nb_2Sn_3$, but no $Nb_3Sn$ or $Nb_2Sn$. In contrast to this, the furnace cooled specimen had a reaction zone predominantly $Nb_3Sn$ with frequent $Nb_2Sn_3$ 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 tin 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 $Nb_3Sn$ (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 $Nb_4Sn$. No $Nb_3Sn$ 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 $Nb_3Sn$ and a bit of $Nb_2Sn_3$ in the $Nb_4Sn$ bands (fig. 8).

After studying the microsections from the various diffusion experiments, the fact became evident that the $Nb_3Sn$ phase can form quite readily from the $Nb_4Sn$ phase on slow cooling. Quenched specimens retain only the $Nb_4Sn$.

As compared with the long diffusion times required to convert niobium particles or wires to $Nb_4Sn$, the conversion of $Nb_4Sn$ to $Nb_3Sn$ 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 $Nb_4Sn$ phase dissolves excess tin, and thus approaches the $Nb_3Sn$ composition.

Evidence of width for the $Nb_4Sn$ phase was obtained by making electron-probe traverses across $Nb_4Sn$ areas on a specimen quenched from 1,200 °C. The analytical values so obtained indicated a composition gradient of about 6 percent within the $Nb_4Sn$ areas. This would place the tentative limits of the $Nb_4Sn$ 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 $Nb_3Sn$ phase.

### 3.6. Thermal Analysis

A specimen of nominal "$Nb_2Sn_3$" 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 863 ±5 °C and were easily detected from the temperature recording. The sample was later prepared for metallographic observation and it exhibited the Nb, $Nb_4Sn$, $Nb_3Sn$, $Nb_2Sn_3$ phases in an excess of Sn (figs. 11, 12).

Additional thermal analyses were run on pressed pellets of "$Nb_3Sn$" 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*

| Sample | Cooling rate | Arrest Temperature | |
|---|---|---|---|
| Compressed "$Nb_2Sn_3$" mixture | 3 °C/min | 917 °C<br>927<br>924 | 859 °C<br>867<br>867 |
| Compressed "$Nb_3Sn$" mixture | 4 °C/min | 743 | |

The thermal analysis data have been interpreted to assign the 863 °C temperature as the peritectic temperature of the $Nb_2Sn_3$ compound and the 922 °C temperature as the liquidus for this composition. The 743 °C arrest on a quick cool is probably near the peritectoid temperature of the $Nb_3Sn$ compound. The results are shown in table 2.

### 3.7. High-Temperature Metallography

In a further attempt to reveal the reactions occurring in this system, a microsection containing a wide vein of $Nb_2Sn_3$ with side veins of $Nb_4Sn$ and $Nb_3Sn$ was removed from the diffusion specimen treated for 200 hr at 700 °C. This section was mounted in the high-temperature stage of a metallurgical microscope in a purified argon atmosphere and kept under observation during a 3-hr heating to an indicated 930 °C.

No significant changes were observed up to 450 °C. However, from this temperature up to 693 °C there were grain-boundary changes in the $Nb_2Sn_3$, and some changes in the $Nb_4Sn$ and $Nb_3Sn$ side veins. At 693 °C the narrow band ($Nb_3Sn+Nb_4Sn$) between the $Nb_2Sn_3$ and the niobium appeared to be more clearly defined and slightly wider. Between 693 and 735 °C a new phase believed to be $Nb_2Sn$ had made its appearance at the Nb—$Nb_2Sn_3$ interface and had grown slightly into both phases. During the course of the heating, the noble-metal thermocouple, located adjacent to the specimen, indicated a brief arrest at 863 °C. As heating continued, this new phase grew until, at 930 °C, it had gradually covered the entire field of view.

At this point, the specimen was given a "gas-quench," resulting in a fairly rapid drop in temperature, probably of the order of 400 °C the first minute.

Microscopic examination of the specimen after removal from the furnace failed to provide further information, due to surface roughness. Also, the usual anodizing procedure failed to give response. As a consequence, the specimen was remounted, very lightly repolished, and then anodized. The structure then revealed a mixture of $Nb_4Sn$ and $Nb_3Sn$ scattered through the niobium grains, with the original vein of solid $Nb_2Sn_3$ terminating as a heavily voided area of dendritic appearance.

### 3.8. General Nature of the System

During the course of these investigations, several generalities have evolved which indicate the type of system under study, as well as some of the difficulties to be anticipated in finally determining the facts concerning the several reactions and their rates. For example, there is considerable evidence that the formation of $Nb_3Sn$, $Nb_2Sn$, and $Nb_2Sn_3$ is a function of the rate of cooling from temperatures above the decomposition temperatures for these compounds. As a consequence, it is essential to the controlled formation of $Nb_3Sn$ that the characteristics of the decomposition reactions be determined.

In this connection, accumulated observations made during the course of these investigations give some indications as to the nature of these reactions. Thus, the unexpected and repeated observance of three or four phases after long-term thermal treatments clearly reveals the sluggishness of some of these reactions. Furthermore, this offers a significant 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 $Nb_2Sn_3$, $Nb_2Sn$, and $Nb_3Sn$. The $Nb_2Sn_3$ 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, $Nb_2Sn_3$ is usually found only at the tips of $Nb_3Sn$ protuberances extending into the tin-rich liquid, or in pockets where tin has been trapped between niobium particles. These structures can be explained if $Nb_2Sn_3$ decomposes thermally at some temperature below 900 °C, and if, at lower temperatures, it reacts with niobium or $Nb_4Sn$ to yield $Nb_3Sn$ and $Nb_2Sn$.

The $Nb_3Sn$ 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 $Nb_3Sn$, including a special powder mixture prepared for this purpose, contained extensive areas of $Nb_3Sn$ 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 $Nb_3Sn$ 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 $Nb_4Sn$, $Nb_3Sn$, $Nb_2Sn$, and $Nb_2Sn_3$, 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 water quenched. Preliminary examinations of these series may be summarized as follows:

Specimens water quenched from 1,000 °C contained *only* niobium, $Nb_4Sn$, and a quenched liquid, not $Nb_2Sn_3$ 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 few very small particles of $Nb_3Sn$ 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 $Nb_2Sn_3$, which apparently was stable at 800 °C. In the lower tin ranges, residual particles of $Nb_2Sn_3$ or quenched liquid apparently had reacted with $Nb_4Sn$ and niobium to form additional particles of $Nb_2Sn$.

Specimens quenched after 21 hr at 700 °C all showed considerable amounts of $Nb_2Sn$, which, however, had not yet replaced $Nb_4Sn$ as the continuous phase. Thus these specimens were reacted *below* the decomposition temperature of $Nb_3Sn$, 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 $Nb_3Sn$ and $Nb_2Sn$ in a matrix of $Nb_4Sn$. There were also a few particles of unreacted niobium. The identity of the $Nb_2Sn$ phase was confirmed in this group of specimens by means of the electron-probe microanalyzer. These results are summarized in table 3.

TABLE 3. *Phases observed in reacted powder mixtures*

Mixtures pressed, reacted at 1,000 °C, and finished by final reaction listed

| Final treatment | | $Nb$ | $Nb_4Sn$ | $Nb_3Sn$ | $Nb_2Sn$ | $Nb_2Sn_3$ | Quenched liquid |
|---|---|---|---|---|---|---|---|
| Temp. | Cooled | L. blue | C. blue | Orient | Aster | Sienna | |
| °C | | | | | | | |
| 1,000 | WQ | + | ++ | (n) | – | – | + |
| 800 | WQ | + | ++ | (n) | – | + | – |
| 740 | Q(1) | + | + | tr | – | + | – |
| 716 | Q(1) | + | + | ++ | – | tr | – |
| 700 | WQ | + | + | + | – | + | – |
| 680 | Q(1) | + | + | + | + | tr | – |
| 600 | F.C. | + | + | + | + | + | – |

(1) Single small pieces of a thermal analysis specimen at 70% Nb, 30% Sn, water quenched. All others are summation of observations on 9 compositions.
(n) Some specimens, particulary those near 35% Sn, showed a few small spots of $Nb_3Sn$ when first examined. Over several weeks, additional particles of $Nb_3Sn$ grew at the interfaces between $Nb_4Sn$ and $Nb_2Sn_3$.
+ Indicates presence.
++ Indicates presence in large amount.
tr Indicates trace.
– Indicates absence.

Thus, the decomposition temperature of $Nb_2Sn_3$ lies between 800 and 1,000 °C, and must of necessity be of the peritectic form, while the decomposition of the desired $Nb_3Sn$ 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 $Nb_3Sn$ into $Nb_4Sn$ and $Nb_2Sn_3$, 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 $Nb_4Sn$). 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. Friability 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 $Nb_3Sn$ 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 $Nb_3Sn$ 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 $Nb_3Sn$ areas.

The $Nb_2Sn_3$ 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 $Nb_3Sn$ 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 wistaria 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 those streamers or a phase of a color approximating wistaria. It is suggested that the probable identity of the streamers may be $Nb_2N$.

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—"$Nb_3Sn$" 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.

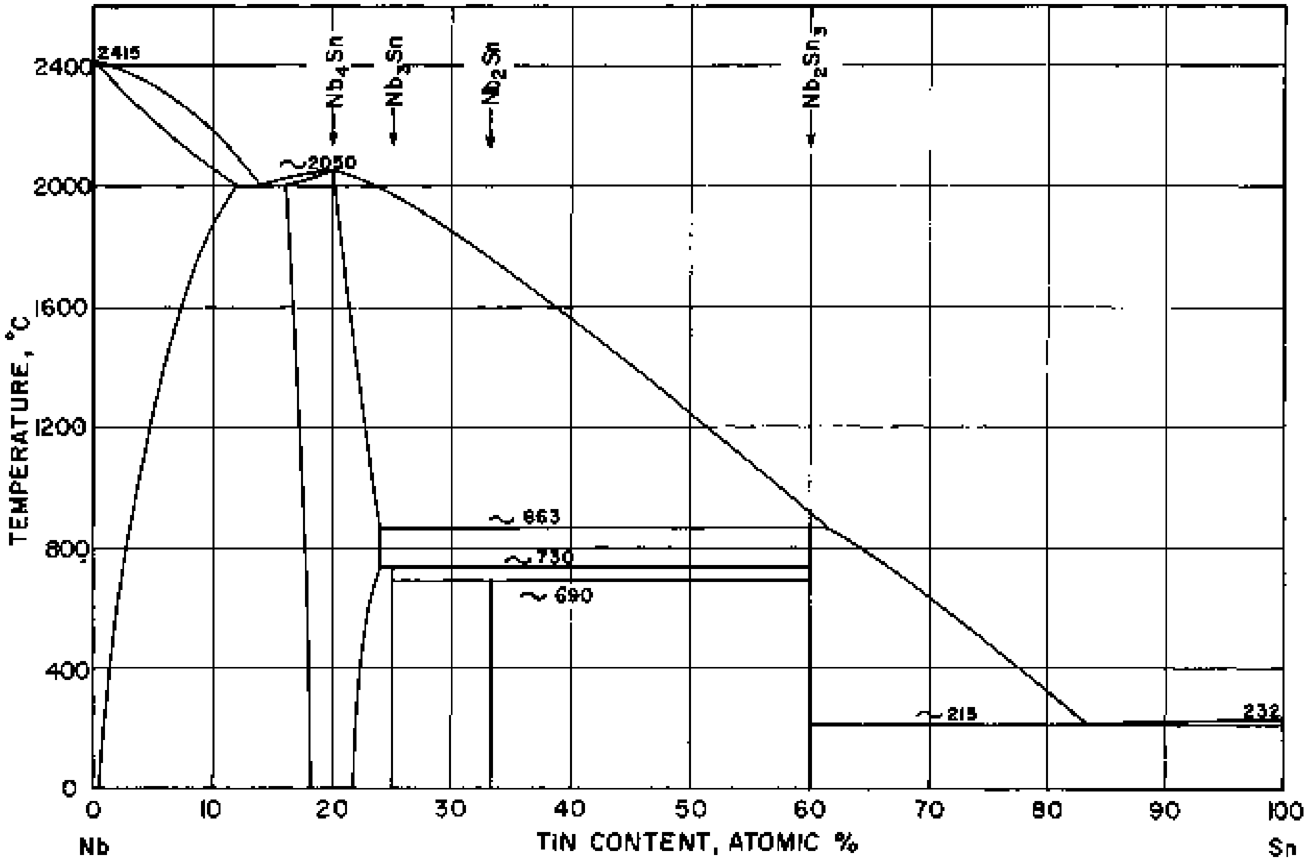

FIGURE 4. *Proposed tentative constitution diagram for the niobium-tin system based on the present NBS study.*

Niobium and tin react quite readily to form $Nb_4Sn$ 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 $Nb_3Sn$ 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, $Nb_2Sn_3$ appears to form quite readily in layers at the $Nb_4$-Sn—Sn interface, with crystals of $Nb_2Sn_3$ growing out into the tin and occasionally becoming detached. By contrast, the $Nb_3Sn$ phase appears only as much thinner layers and is usually discontinuous.

This configuration can be expected when one realizes that the $Nb_3Sn$ 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 $Nb_3Sn$ 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 $Nb_2Sn_3$, or excessive reaction of niobium, which will produce mainly $Nb_4Sn$. 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 $Nb_3Sn$, either by fusion methods or by complete interaction of niobium and tin powders, involves first forming a mixture of $Nb_4Sn$ and $Nb_2Sn_3$, followed by a peritectoid reaction between these products to form the $Nb_3Sn$.

The application of these phenomena to practical wire fabrication could take two distinct forms. If a continuous network of $Nb_3Sn$ 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 $Nb_3Sn$. 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 $Nb_3Sn$ 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 $Nb_4Sn$ and residual liquid. This mixture may then subsequently be annealed in the range 600 to 700 °C until the peritectoid conversion to $Nb_3Sn$ is complete.

Probably the most significant practical result of this investigation will be to clarify the fact that the desired $Nb_3Sn$ 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 predicated from the results thus far obtained in the current investigations.

The intermetallic compound $Nb_3Sn$, which appears to be the desirable constituent for superconducting purposes, occurs between the compounds $Nb_4Sn$ and $Nb_2Sn_3$, which are stable to considerably higher temperatures. At lower temperatures, the system is further complicated by the formation of $Nb_3Sn$.

This seriously complicates the problem of attaining either a continuous body of homogeneous $Nb_3Sn$ 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

[1] J. E. Kunzler, E. Buehler, F. S. L. Hsu, and J. H. Wernick, Superconductivity in $Nb_3Sn$ at high current density in a magnetic field of 88 Kgauss, Phys. Rev. Letters 6, 89, (1961).
[2] V. D. Arp, R. H. Kropschot, and J. H. Wilson, Superconductivity of $Nb_3Sn$ in pulsed fields of 185 kilogauss, Phys. Rev. Letters 6 (9), 452, (1961).
[3] B. T. Matthias, T. H. Geballe, S. Geller, and E. Corenzwit, Superconductivity of $Nb_3Sn$, Phys. Rev. 95, 1435, (1954).
[4] E. M. Savitskii, M. I. Agafona, and V. V. Baron, The structure and properties of niobium-tin alloys, Izvest. Akad. Nauk S.S.S.R. Met. i Toplivo (Teklin) 1959 (5) 138–141 (in Russian).
[5] M. L. Picklesimer, Anodizing as a metallographic technique for zirconium base alloys, United States Atomic Energy Commission ORNL—2296, 13pp., (1957).
[6] A. Maerz and M. R. Paul, Dictionary of Color, McGraw-Hill Book Company, Inc., New York, New York (1930).
[7] J. R. Cuthill, L. L. Wyman, and H. Yakowitz, Metallurgical microanalysis by means of the electron probe, (in preparation).
[8] G. A. Moore, L. L. Wyman, and H. M. Joseph, Comments on the possibilities of performing quantitative metallographic analysis with a digital computer. Ch. from Quantitative Metallography, F. N. Rhines Ed. McGraw-Hill Co., in Press.

# LEGEND

| PHASE | DESIGNATION[+] | LOCATION | COLOR |
|---|---|---|---|
| Nb | Light Beryl Blue | Plate 33; E-1 | 🟦 |
| $Nb_4Sn$ | Calamine Blue | Plate 33; J-2 | 🟦 |
| $Nb_3Sn$ | Orient | Plate 36; D-11 | 🟦 |
| $Nb_2Sn$ | Purple Aster | Plate 43; J-7 | 🟪 |
| $Nb_2Sn_3$ | Burnt Sienna | Plate 5; F-12 | 🟧 |
| Sn | Chrome Lemon | Plate 9; K-2 | 🟨 |
| Impurity | Wistaria | Plate 41; E-8 | 🟪 |

[+] See ref. 6

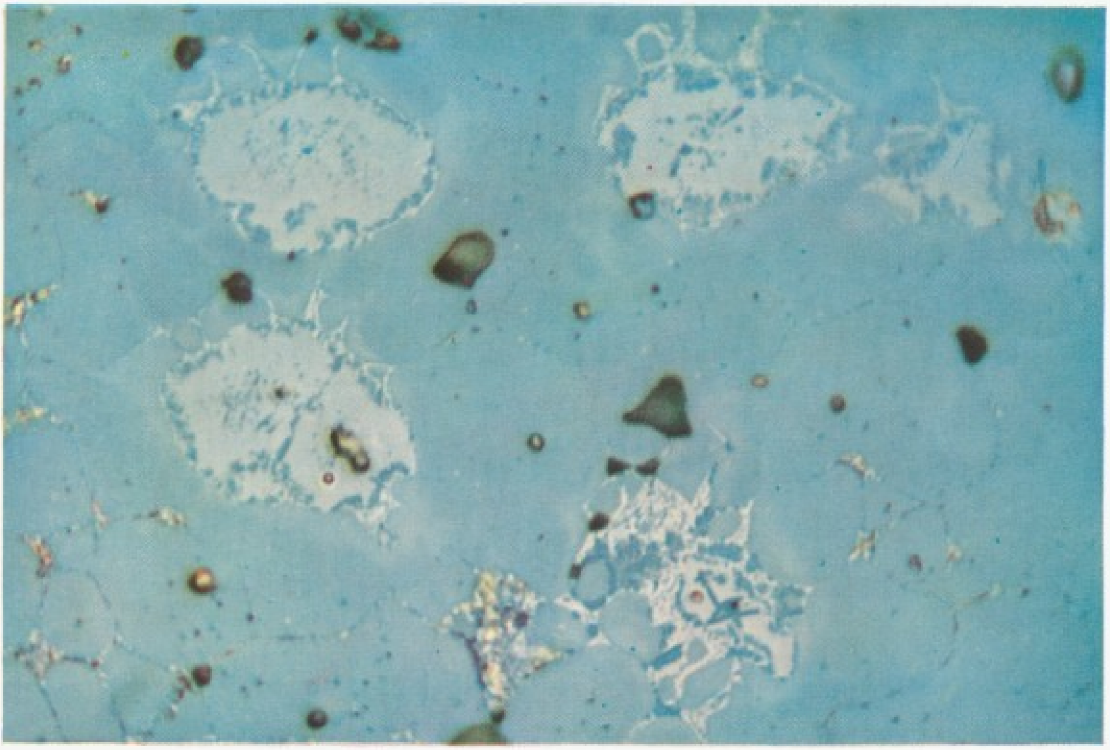

FIGURE 5. *Eutectic type structure developed between some free niobium and* $Nb_4Sn$ *after reheating a specimen of nominal 80%* Nb—*20%* Sn *composition quenched from 800, to about 1,850 °C.*

The matrix is $Nb_4Sn$. X1000.

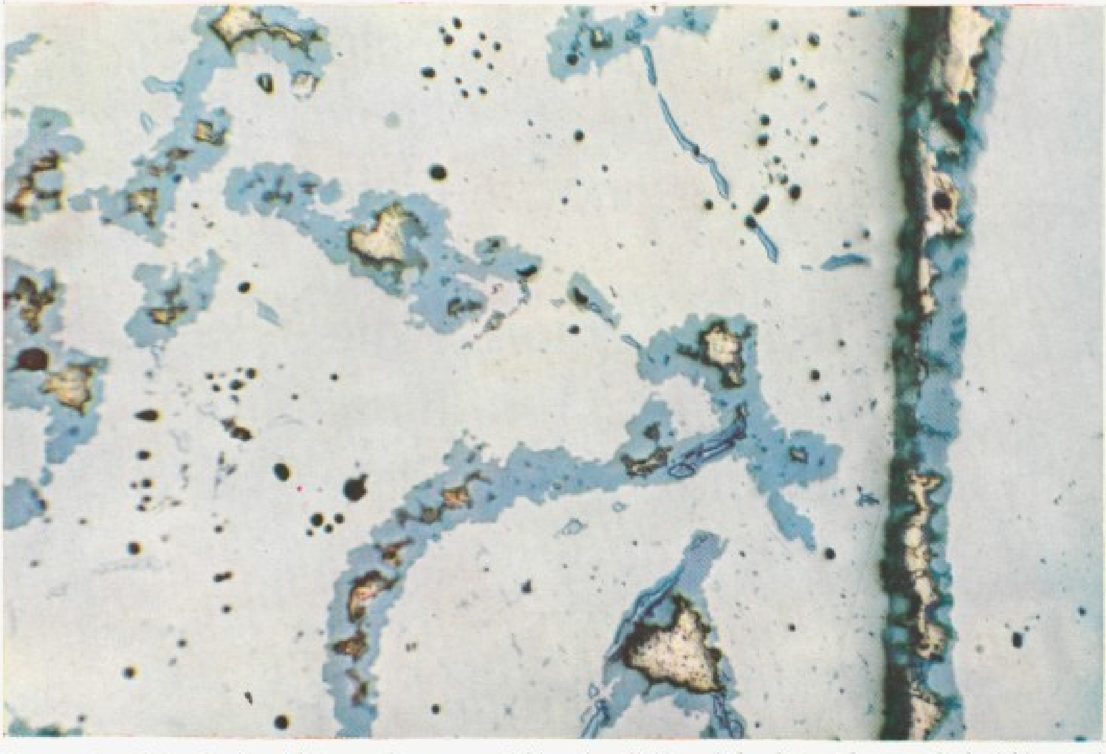

FIGURE 6. *Joint developed between the porous niobium bar (left) and the electron beam melted niobium rod (right).*

X100.

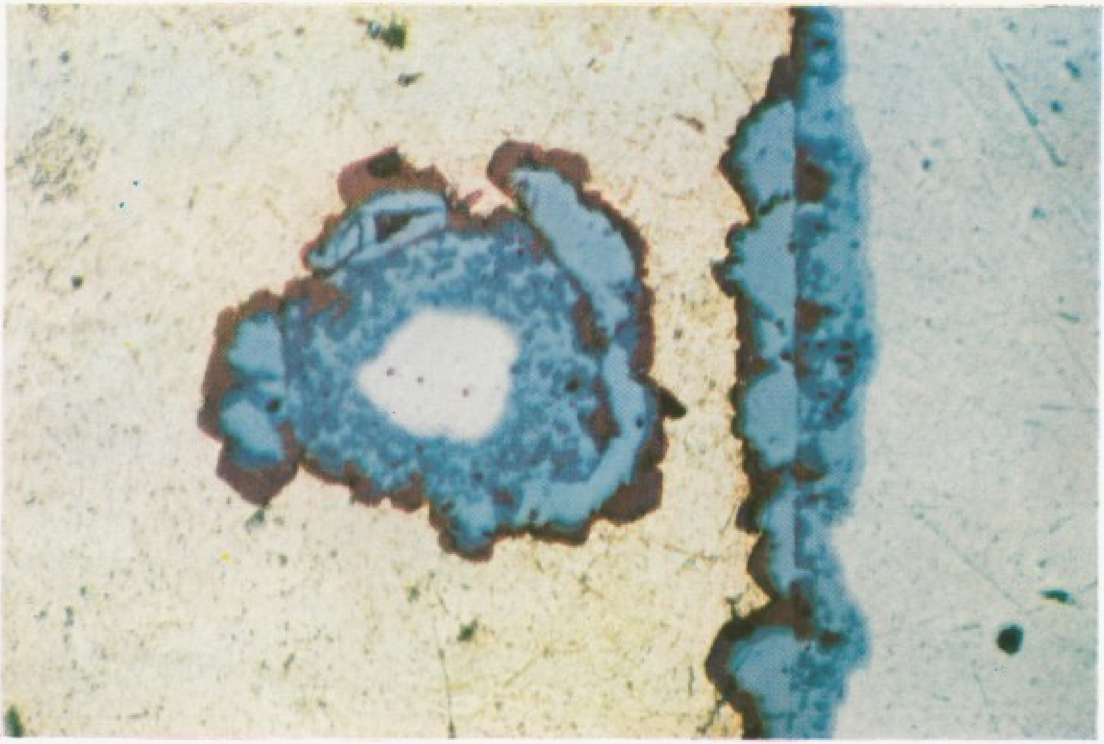

Figure 7. *Cross section of a nominal 0.004-in. niobium wire heated for 8 hr at 1,000 °C in a bath of molten tin and furnace cooled.*

The niobium shell is at the right. X500.

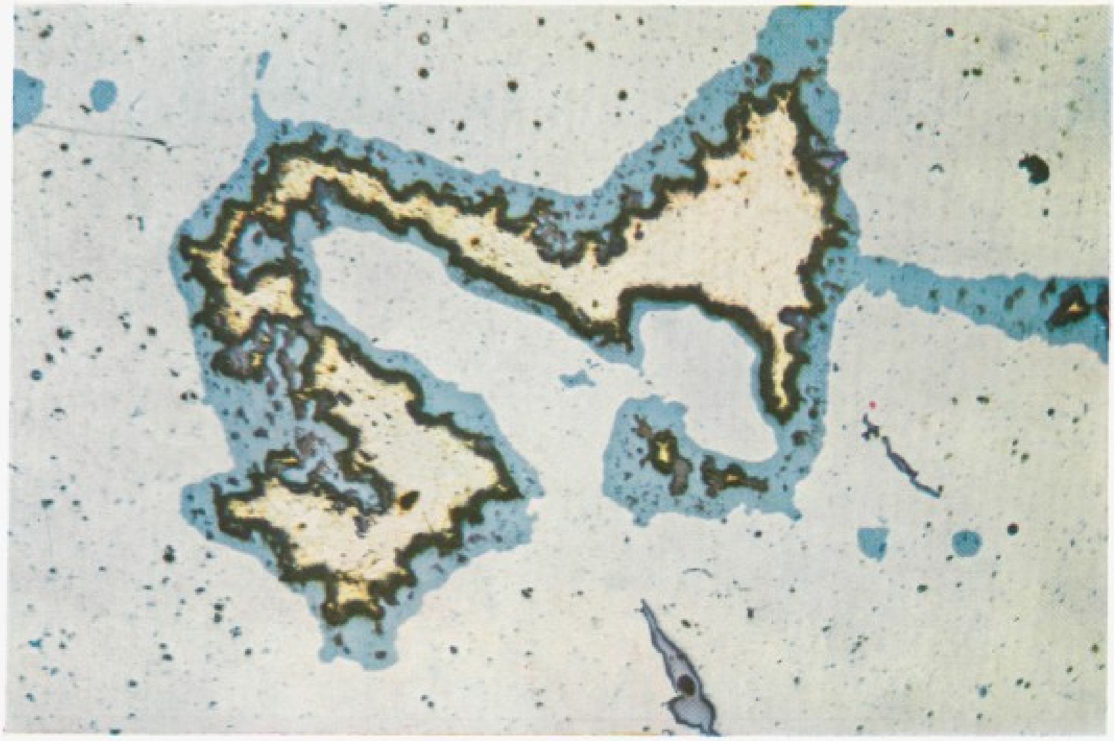

Figure 8. *Interior of porous niobium bar after diffusion in a bath of molten tin for 16 hr at 1,000 °C followed by furnace cooling.*

X200.

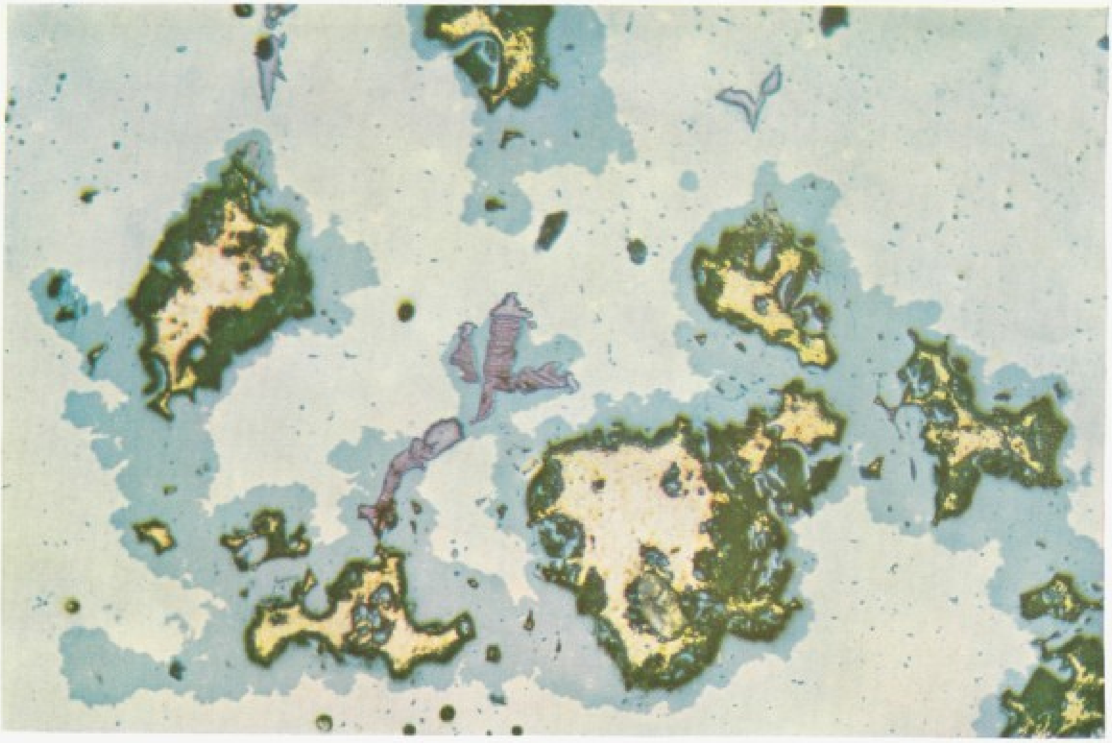

**FIGURE 9.** *Interior of porous niobium bar after diffusion in a bath of molten tin for 32 hr at 1,200 °C followed by water quench.*

X200.

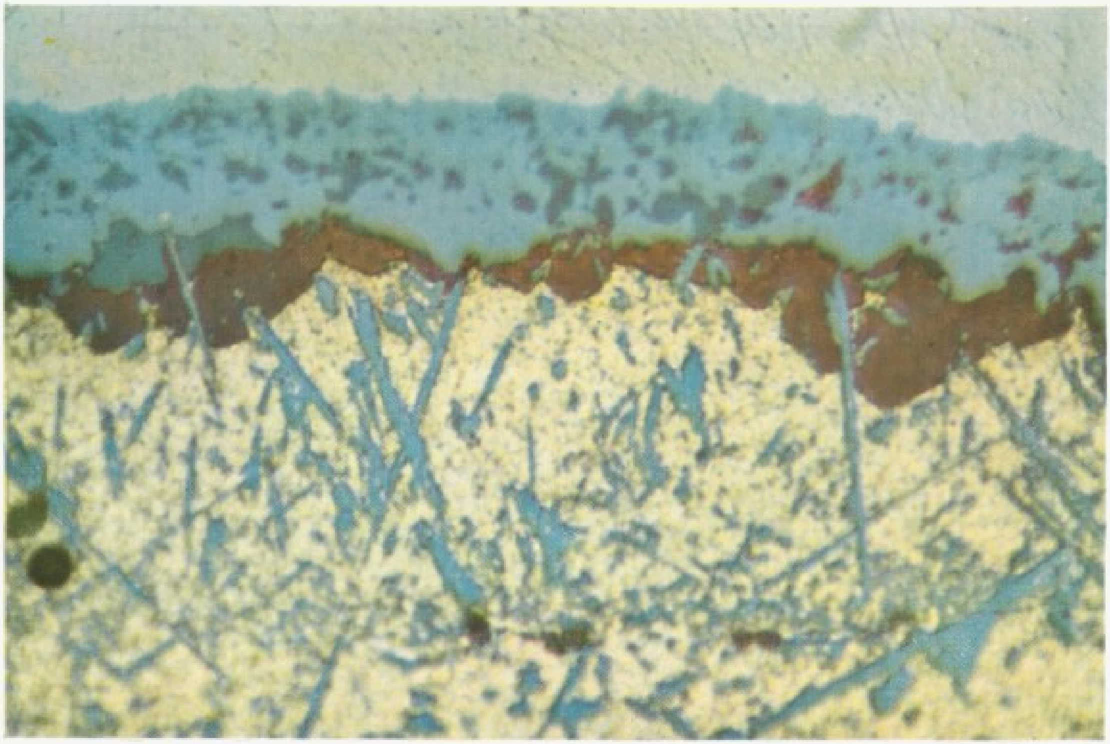

**FIGURE 10.** *Exterior of niobium shell after diffusion in a bath of molten tin for 8 hr at 1,000 °C followed by furnace cooling.*

The needles are $Nb_4Sn$. X1000.

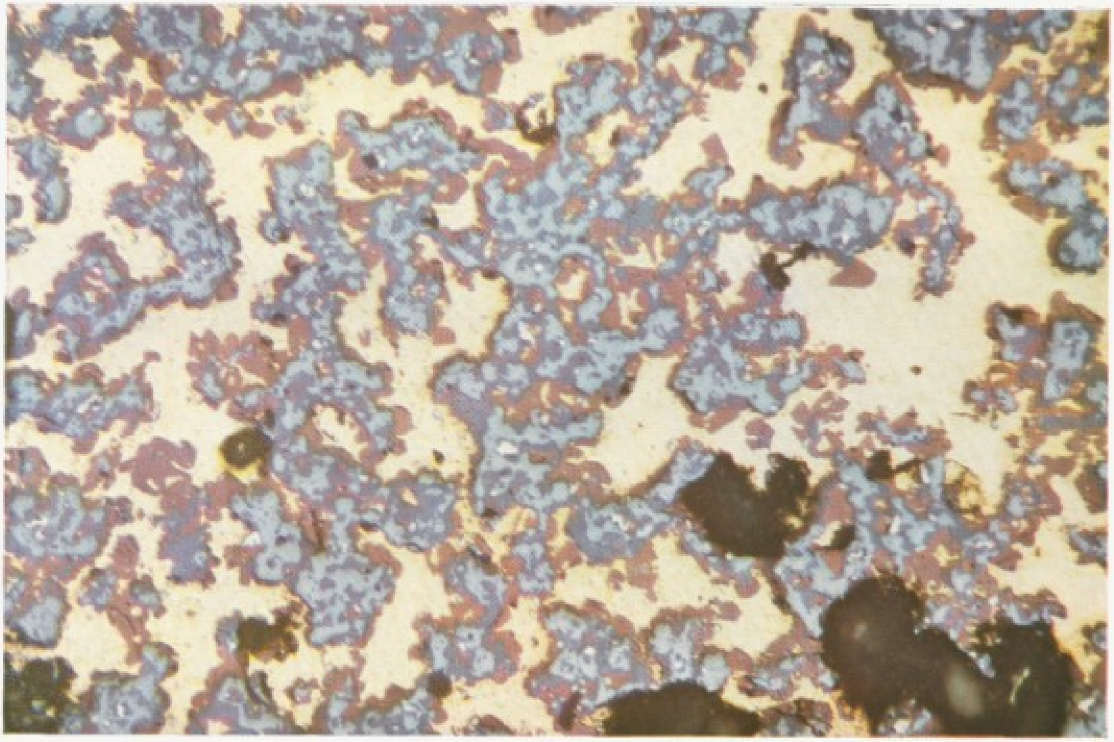

FIGURE 11. *Interior of thermal analysis specimen (nominal* $Nb_2Sn_3$ *hot pressed pellet) after heating to 1050 °C at 3 °C/min followed by cooling to room temperature also at 3 °C/min.*

X200.

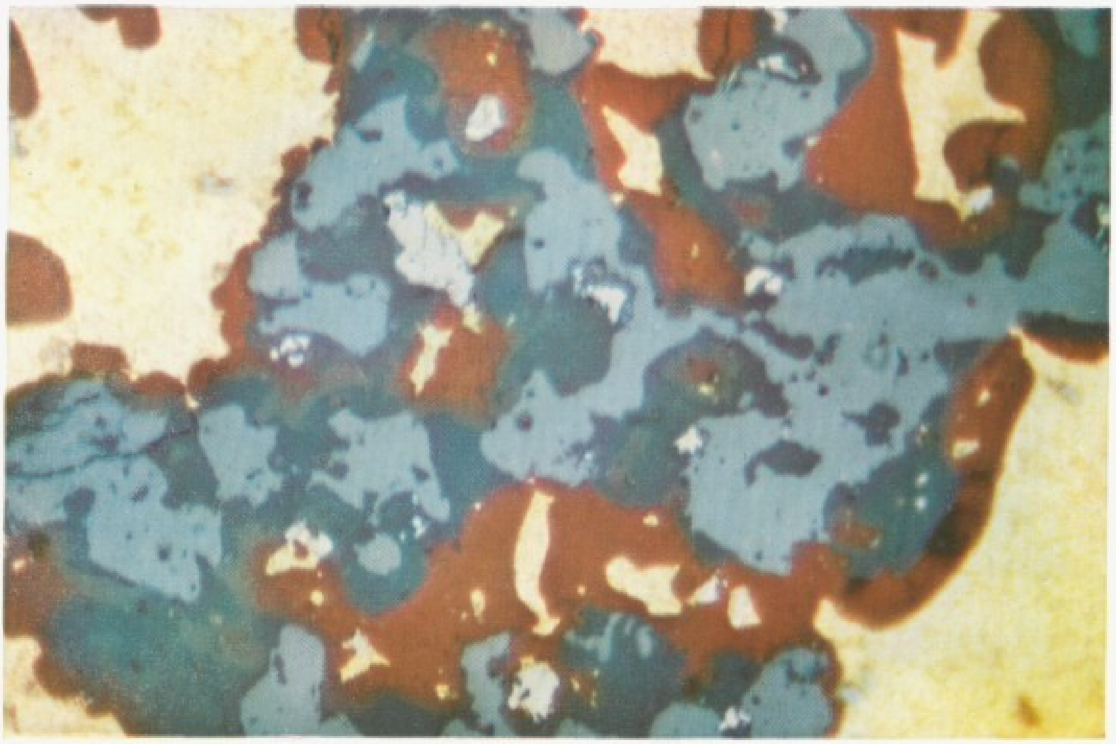

FIGURE 12. *Interior of thermal analysis specimen (nominal* $Nb_2Sn_3$ *hot pressed pellet) after heating to 1,050 °C at 3 °C/min followed by cooling to room temperature also at 3 °C/min.*

X1000.

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