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A POWDER ROLLED SUPERCONDUCTING  
COMPOSITE WITH CONTROLLED MORPHOLOGY

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ABSTRACT

A procedure is described for producing a superconducting tape by powder metallurgy techniques. Although the superconducting phase,  $Nb_3Sn$ , is inherently brittle, it is shown how flexibility is achieved by thermo-mechanical treatments that cause this phase to occur as interconnected filaments dispersed in a ductile matrix of niobium.

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## I. INTRODUCTION

In modern technology there is a continuing need for materials with unique properties. Not infrequently a desired property is accompanied by an undesirable one, such as brittleness, that makes fabrication into useful forms impossible by conventional methods. In these instances special procedures must be devised. Just such a situation exists in the field of superconductivity.

One of the best superconducting materials is the intermetallic compound,  $Nb_3Sn$ , discovered in 1954 by Matthias and his co-workers.<sup>1</sup> This material can sustain a current density of the order of 100,000 amperes per square centimeter in a magnetic field of 88 k Gauss, at 4.2°K, as was first noted by Kunzler, et al.<sup>2</sup> in 1961. However,  $Nb_3Sn$  is an extremely brittle material. In order to make effective use of its extraordinary superconducting properties, it is necessary to have it available in the form of tape or wire. Clearly this requires imaginative approaches to the problem of fabrication. J. E. Kunzler<sup>3</sup> has reviewed some of the early efforts, including the cored-wire process developed at the Bell Telephone Laboratories, and the thin layer coating of the Radio Corporation of America produced by vapor decomposition. The manufacture of solenoids from some of these materials required that the reaction between niobium and tin be carried out after the winding was completed—a costly and inconvenient procedure. A flexible tape with  $Nb_3Sn$  present as a thin layer obtained by a diffusion process has been described by M. G. Benz.<sup>4</sup> A new approach to this problem is presented herein which results in a flexible composite with the brittle phase in the form of thin, interconnected filaments dispersed in a ductile matrix. The filaments have a thickness of approximately 2 microns.

To obtain this composite, niobium powder was roll-compacted and sintered to produce a tape permeated by a capillary system of interconnected pores. The porous tape was infiltrated with tin and then given a diffusion heat treatment to form the desired  $Nb_3Sn$  phase. It was found, however, that the infiltrated tape was sufficiently malleable to permit a considerable reduction in thickness by cold rolling prior to the heat treatment and that by using a thermo-mechanical processing sequence it was possible to obtain a composite with an increased volume fraction and an improved morphology of the brittle  $Nb_3Sn$  phase.

A survey was made of the important process variables such as powder characteristics, powder-rolling parameters, sintering and infiltration conditions, amount of cold reduction, and the time, temperature and environment required for the diffusion heat treatment. The composites were studied metallographically, using for phase identification the characteristic colors obtained by anodic etching. In a few instances the identification was verified by x-ray diffraction. The composition of the  $Nb_3Sn$  phase was determined by the electron beam microprobe technique. Scanning electron microscopy was used for powder characterization.

## II. MATERIALS AND EQUIPMENT

### A. Niobium Powder

The niobium powder was supplied by the Wah Chang Albany Corporation. The major impurities, in parts per million, were as follows: oxygen, 1780; tantalum, 380; iron, 230; tungsten, 110; and carbon, 70. This powder was produced by the hydride-dehydride process from slabs of electron beam melted ingots. Although designated by the manufacturer as -270 mesh, it was found that nearly all of the powder was -325 mesh, and that 70% was -400 mesh. A micro-sieve analysis of the -400 mesh portion gave almost equal percentages of the particle size fractions -400 + 500, -500 + 750, - 750 + 1000, and -1000 mesh. Figure 1, a scanning electron micrograph, shows the large range of particle sizes in the as-received powder, and also the angular and irregular shape of the particles (an important factor in obtaining good green strength).

### B. Powder Rolling Mill

The mill used for powder rolling is shown in Fig. 2. It has 2-inch diameter hardened steel rolls, and is powered by a continuously variable speed motor drive, providing a range of roll speeds from 2 to 20 RPM. To prevent lateral spread<sup>5</sup> of the powder and provide edge retention for the rolled strip, grooves 1/8-inch wide and 1/8-inch deep were ground into the rolls, leaving between the grooves the desired width of rolling surface. Two side retainers of 1/8-inch thick plexiglas were machined to straddle the rolls, fitting in the grooves and resting on the reduced diameters, thus confining the powder laterally throughout the roll bite. The plexiglas hopper, made to fit the side retainer

assembly, has an adjustable slide to regulate the powder flow and maintain an adequately constant powder head. Roughening the rolling surfaces with a fine abrasive significantly improved the uniformity of roll compaction.

### C. Sintering and Infiltrating Facilities

The operations of sintering and infiltrating were carried out in a two-compartment apparatus which was convenient for experiments with short samples. The upper section is a stainless steel, vacuum-tight chamber containing a cylindrical tungsten mesh element that was heated resistively. The heating element was surrounded by several concentric radiation shields made of tantalum. Temperatures up to 2350°C could be attained in a few minutes, and were monitored by means of both a tungsten-rhenium thermocouple and an optical pyrometer. A 2-inch diameter quartz tube with a closed bottom was attached to the lower flange of the sintering furnace, using 'O' ring seals. Inside the quartz tube was a graphite crucible containing a bath of molten tin. The temperature of the bath was maintained by an automatically controlled nichrome furnace surrounding the lower end of the quartz tube.

To accomplish sintering and infiltration, a length of green tape was suspended from a rod that passed through a vacuum seal in the upper flange of the sintering furnace. The tape was held in the hot zone for the desired sintering time, and then, after cooling, was lowered into the tin bath for infiltration.



### III. PROCESSING OF COMPOSITE

#### A. Roll Compaction of Niobium Powder

In order to obtain tape with a green strength adequate for handling, and, at the same time, a porosity of approximately 30%, several more or less interrelated variables required investigation. These included powder characteristics, roll gap, roll speed, surface condition of the rolls and the use of additives. The principal effect of roll diameter is to limit the maximum obtainable tape thickness. The 2-inch diameter rolls incorporated in the available mill imposed a maximum tape thickness of approximately 0.025 inches.

All of the powders employed had the angular, irregular shape shown in Fig. 1. Coarser powders, such as -100 +200 mesh and -200 +325 mesh, permitted continuous compaction in only a very narrow range of rolling conditions, and the resulting tape exhibited jagged edges and a tendency to develop cracks. The -270 mesh powder described in Section II produced tape with a good surface appearance at roll speeds from 2 to 20 RPM and with roll gaps from 0.010 inches to 0.018 inches. With a given roll speed, a decrease in roll gap led to a decrease in porosity and an increase in green strength. The effect of increasing the roll speed while the roll gap was held constant was to diminish the green strength and increase the porosity. With this powder a good balance between porosity and green strength was achieved under the following conditions: roll speed, 5 RPM; roll gap, 0.016 in.; tape thickness, 0.022 in. The green tape had a porosity of 30% and could support 830 in. of its own weight.

A simple, saturated gravity feed of the powder was augmented by vibrating the hopper to assure uniformity of powder flow. It was found that no appreciable compaction occurred with polished rolls. However, when the rolls were roughened with 240 grit abrasive, tape of good quality was obtained. The addition to the powder of a binding agent such as methyl cellulose was observed to provide several advantages, among which were an improvement in the surface appearance of the green tape, a decrease in the tendency toward edge cracking, successful compaction with larger roll gaps, and greater flexibility of the green tape. However, a definite disadvantage was the complication of the subsequent sintering operation. The rate of heating had to be carefully controlled to avoid blistering, and the niobium was embrittled by even small amounts of residue. Consequently, no additives were used.

#### B. Sintering and Infiltrating

The overall properties of the tape were established by the sintering time, temperature and environment. These parameters were constrained to a rather narrow range by the simultaneous requirement of ductility and porosity. Sintering for 3 minutes at 2225°C in a vacuum of  $< 4 \times 10^{-5}$  Torr provided a practical compromise; the tape thus processed had a porosity of about 25% and could sustain a bend of 0.1 in. radius. Sintering in a purified inert gas atmosphere gave unsatisfactory results with respect to ductility.

Infiltration was accomplished by immersion of the sintered tape for one minute in a tin bath which was maintained at a temperature of 650°C. At temperatures lower than 550°C there was either partial or no infiltration. For appreciably longer times at 650°C, or at higher

temperatures, intermediate phases were formed with an embrittling effect that severely limited the amount of cold work that could be performed. The microstructure of tape infiltrated by one minute immersion at 650°C exhibited virtually no intermediate phase, only niobium and tin being visible in the microstructure. This was consistent with the observation that the ductility was not diminished.

#### C. Cold Rolling Infiltrated Tape

Increasing amounts of deformation produced progressive changes in the morphology of the infiltrated tin, leading to a filamentary structure which greatly extended the interfacial area between the niobium and tin. This had an important influence on both the effectiveness of the diffusion heat treatment and the morphology of the resulting  $Nb_3Sn$  phase (on which the flexibility of the finished tape was strongly dependent). Due to the difference in flow stress of the two metals, tin was squeezed out to the surface to an excessive degree after reductions in the order of 95%. Therefore to maintain an adequate volume fraction of tin the reduction was limited to a maximum of 85% with the usual amount being 75%.

#### D. Diffusion Heat Treatment

The desired superconducting phase is  $Nb_3Sn$ . Two additional intermediate phases occur in the niobium-tin system,  $NbSn_2$  and  $Nb_6Sn_5$ . Neither of the latter is of value for superconductivity--their critical temperatures<sup>6,7</sup> are of the order of 2°K compared with 18.5°K for  $Nb_3Sn$ . Both are quite brittle. According to the alloy diagram<sup>7</sup> for the niobium-tin system, shown in Fig. 3, both of these phases are unstable at temperatures above approximately 930°C. The diffusion treatments were therefore carried out in the temperature range 950-1000°C, either in an

inert gas or in a molten tin bath--the latter provided the additional advantage of leaving a good tin coating that facilitated soldering. The heat treatments were quite short--generally less than 3 minutes. By controlling the amount of prior deformation, and the time and temperature of this heat treatment, part or substantially all of the infiltrated tin could be converted to  $Nb_3Sn$ .

#### IV. RESULTS AND DISCUSSION

In this section, photomicrographs are presented that show the structure of the composites, and the control that can be achieved over the volume fraction and morphology of the desired intermediate phase. A length of tape was roll-compacted from the as received -270 mesh niobium powder, sintered and infiltrated with tin, all within the range of conditions described in the preceding sections. A portion of the tape in the as infiltrated condition, along with two portions that were given a 50 and 75 per cent reduction in thickness respectively, were simultaneously heat treated for approximately one minute at 1000°C. The resulting structures are shown in Fig. 4. With the anodizing conditions used (a modification of Picklesimer's procedure)<sup>8</sup>, characteristic colors were obtained for the various phases, as follows: niobium, light blue; tin, white;  $Nb_3Sn$ , dark blue; and  $Nb_6Sn_5$ , reddish brown. Figure 4a shows that in the as infiltrated condition only the primary phases, niobium and tin, are present. Due to the very short heat treatment period of one minute, some  $Nb_6Sn_5$  may be seen along with  $Nb_3Sn$  in Figs. 4 (b), (c) and (d). The latter three figures show rather convincingly the effects of increasing amounts of deformation on

reducing the volume fraction of residual tin, producing a progressively more filamentary type structure, and increasing the volume fraction of  $Nb_3Sn$  for a given heat treatment. If, for the sample with the 75% reduction in thickness, shown in Fig. 4 (d), the heat treating time was increased to about 3 minutes, virtually no unreacted tin would remain, and only the two phases, niobium and  $Nb_3Sn$ , would be present.

Some interesting comments can be made in regard to Figs. 4 (b), (c) and (d). After a short (1-3 minutes) diffusion heat treatment the volume fraction of  $Nb_3Sn$  in a tape that had a prior deformation of 75% was found to be more than twice that of a tape with a 50% prior reduction. The question might be raised as to why not increase the period of heat treatment until all of the tin had reacted, leading to equal volume fractions for all three cases. For one thing the time required to complete the reaction can be quite long. An as infiltrated sample that had been heated for 16 hours at  $1000^\circ C$  still showed some unreacted tin, as may be seen in Fig. 4 (e). For another, brittleness becomes a serious problem. The sample that had been heated for 16 hours could be handled only with the utmost care. It has been found that if the thickness of the  $Nb_3Sn$  phase exceeds 5-6 microns the tape becomes brittle. The thickness of the  $Nb_3Sn$  filaments in Fig. 4 (d) is approximately 2 microns. Tape having this microstructure can be wrapped, unwrapped and then reverse wrapped around a one-inch diameter mandrel with no apparent damage to the filaments. This is an important feature of a superconducting material that is to be used for the winding of magnet coils.

Several aspects of the procedure that has been described—notably, the use of rolling as the means of compaction, and the short cycle thermal treatments for sintering, infiltration and reaction—suggest the feasibility of a continuous operation, as shown schematically in Fig. 5 . This potentiality is the subject of continuing investigations in the course of which the correlations and optimum ranges of the process variables will be determined more explicitly.

The superconducting properties of this composite tape and the test procedures used for their determination will be presented in another report. It may be briefly noted here, however, that the filaments exhibit a critical temperature and critical current density characteristic of  $Nb_3Sn$ .

#### ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Fig. 1. Scanning electron micrograph of as received -270 mesh niobium powder. X250

Fig. 2. Mill for rolling niobium powder.

Fig. 3. Niobium-tin equilibrium diagram.<sup>8</sup>

Fig. 4. Porous niobium tape infiltrated with tin.

Light blue: Niobium; White: Tin; Dark Blue:  $Nb_3Sn$ ;

Reddish Brown:  $Nb_6Sn_5$ .

a) As infiltrated. X400

b) Infiltrated and heated for one minute at 1000°C. X1500

c) Infiltrated, cold rolled to 50% reduction in thickness and heated for one minute at 1000°C. X1500

d) Infiltrated, cold rolled to 75% reduction in thickness and heated for one minute at 1000°C. X1500

e) Infiltrated and heated for 16 hours at 1000°C. X400

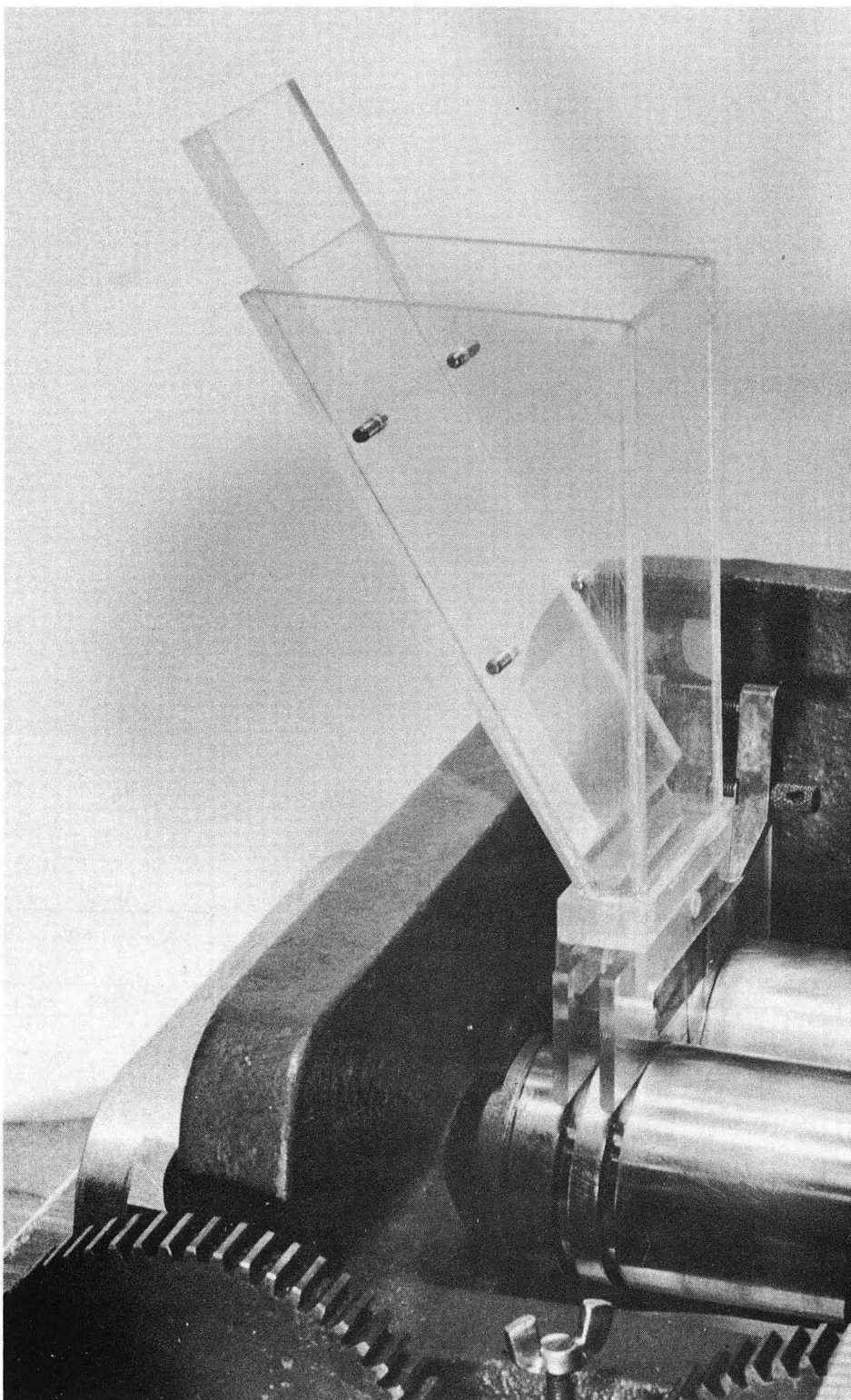
Fig. 5. Schematic representation of a continuous system for making a Nb-Nb<sub>3</sub>Sn composite tape from niobium powder.





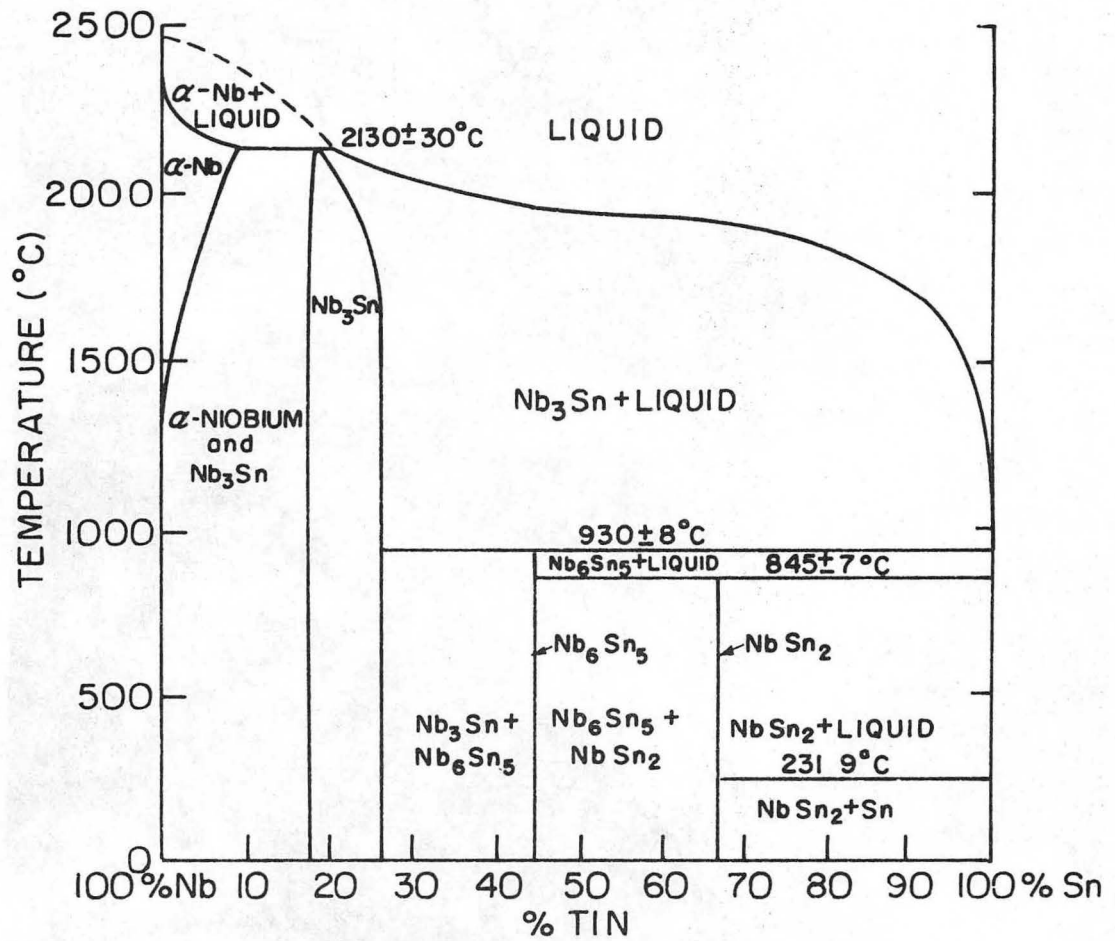
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Fig. 1



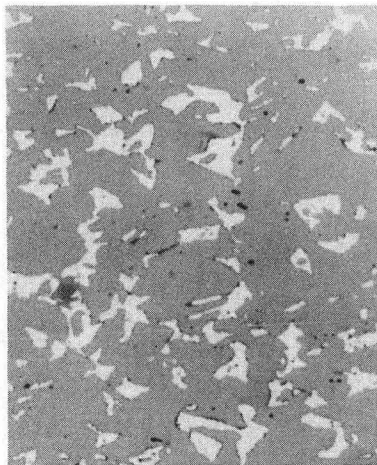
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Fig. 2

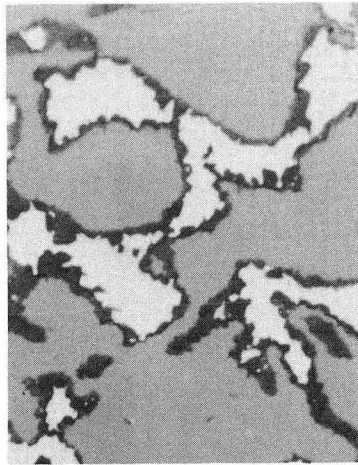


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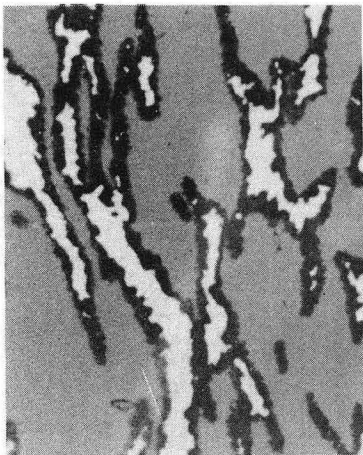
Fig. 3



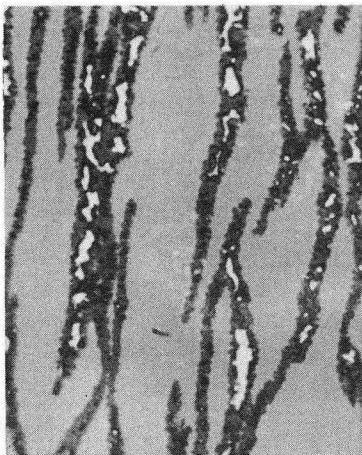
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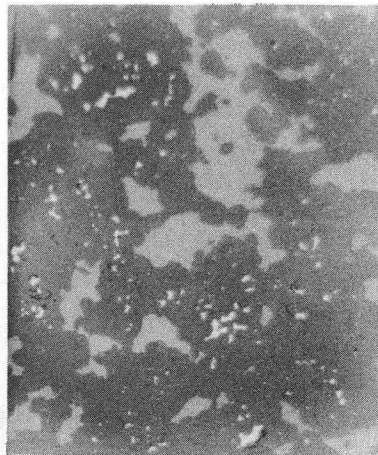
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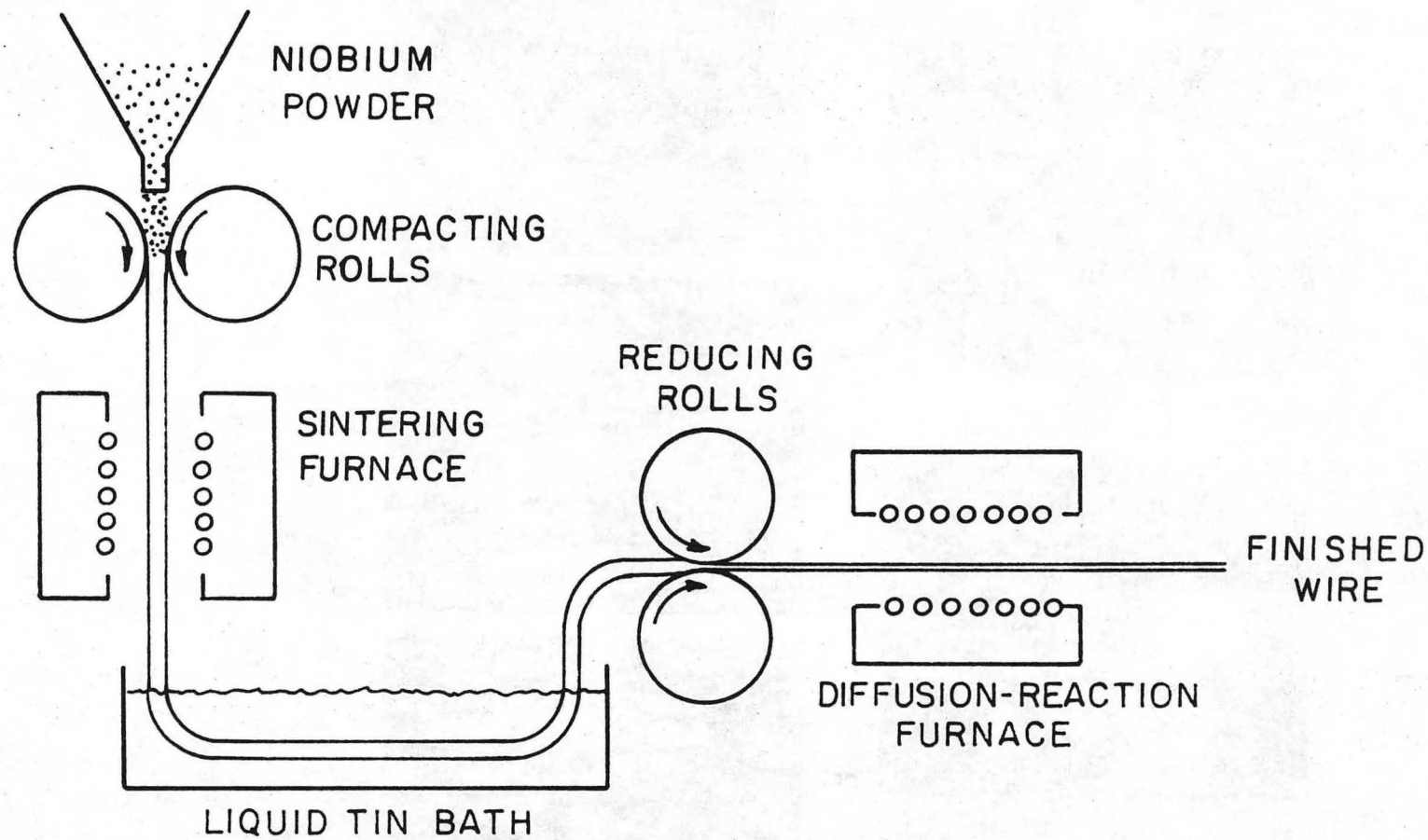
**D**



**E**

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Fig. 4



XBL 721-5992

Fig. 5

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