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EFFECT OF THE MICROSTRUCTURE ON THE SUPERCONDUCTIVE PROPERTIES OF Nb3Sn IN A NbC MATRIX.

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Jean Chabanne
(M.S. Thesis)

September 1967

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EFFECT OF THE MICROSTRUCTURE ON THE SUPERCONDUCTIVE PROPERTIES OF Nb₃Sn IN A NbC MATRIX

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EFFECT OF THE MICROSTRUCTURE ON THE SUPERCONDUCTIVE PROPERTIES OF Nb\textsubscript{3}Sn IN A NbC MATRIX

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ABSTRACT

Various hot-press processing of powder of Nb, Sn, C starting with different compositions have been attempted. The sintered product consists of grains of NbC surrounded by Nb\textsubscript{3}Sn.

Critical temperature measurements, x-ray diffraction, microprobe investigations and critical field ($H_{c2}$) measurements in a pulsed field at 4.2°K have been made.

A critical field of 240 kG at 4.2°K (J perpendicular to H) has been obtained by extrapolation for one of the samples. The current density was still 5000 A/cm\textsuperscript{2} at 203 kG.

We have been looking for the best parameters (composition of the powder, sintering processing) which will lead to the best critical field-critical current curve.

Section I: The introduction describes previous ways of manufacturing Nb\textsubscript{3}Sn and what we have been attempting in this work.

Section II: Hot press processing deals with our method of fabrication.

Section III: This section describes the variation of structure versus composition and versus heat treatment.

Section IV: Gives the $T_c$ results and correlates them to the heat treatment.

Section V: Gives the $H_{c2}$ results.
Section VI: Conclusion stresses the positive results, the questions which are still unsolved, and possible paths for future research.
I. INTRODUCTION

Since the discovery of the B-tungsten structure compound \( \text{Nb}_3\text{Sn} \) by Matthias et al. (1954),\(^{26}\) it has been the best superconductor known. It displays the highest \( T_c: 18^\circ\text{K} \) and a high critical field limit (\( H_{c2} \) has been found up to 240 kG, for \( T = 0^\circ\text{K} \)). In May of 1967, thirteen years later, Matthias et al. came out with a solid solution between \( \text{Nb}_3\text{Al} \) and \( \text{Nb}_3\text{Ge} \) whose critical temperature is \( 20^\circ\text{K} \).\(^1\) No data concerning critical fields were given.

Many methods of making \( \text{Nb}_3\text{Sn} \) have been tried successfully, either for research or for industrial purposes. To quote the most important let us give the following methods:

- Simultaneous evaporation and condensation of the two metals in the correct proportion,\(^2\)
- Chemical formation by reduction on a substrate of chloride gas of \( \text{Nb} \) and \( \text{Sn} \) by hydrogen,\(^3\)
- Sintering of \( \text{Nb} \) and \( \text{Sn} \) powder either alone or in a \( \text{Nb} \) wire,\(^4\) and
- Formation of a diffusion layer by annealing of a \( \text{Nb-Sn} \) sandwich, previously cold-rolled.\(^5\)

This last method is presently being used on an industrial scale. General Electric is marketing a "diffusion processed Niobium Tin tape" which can yield, when in the shape of a coil a magnetic field up to 100 kG at \( 4.2^\circ\text{K} \).\(^5\)

The \( \text{Nb}_3\text{Sn} \) configuration (a thin layer 2 to 3μ thick in between \( \text{Nb} \) and \( \text{Sn} \)) allows the manufacturer to cope easily with the extreme brittleness of the \( \text{Nb}_3\text{Sn} \) compound.

Our approach has been a different one and was suggested by the results of J. Olson's work.\(^{25}\) We started with a powder of carefully
mixed Nb, Sn and C which was sintered in a hot press at various temperatures (from 1450°C to 2200°C) and different times (from 8 min to 60 min). In every case we got a two-phase product consisting of grains of NbC surrounded by a continuous phase of mostly Nb3Sn. (See plates 1 to 17.)

We have tried to control the thickness of the Nb3Sn grain boundary phase and to act on its structure through the starting composition of the powder and the hot-press processing. Our aim was to improve the critical current and critical field (J and Hc2) characteristic of our samples.

Hc2 and Jc in an even more pronounced manner are known to be structure sensitive and are dependent upon the normal state resistivity \( \rho \) through the structural defects. Moreover Hc2 is known to be dependent on the thickness of the superconductor \( d_c \) when the thickness is lower than a critical value \( d_c = 2\sqrt{5\lambda/k(t)} \), which in this case will be about 250 Å. With this method it seems difficult to get down to this small range. The thinner grain boundaries we obtained were around 1000 Å (see plates 10,11,12). One can question the continuity of such a layer with such a small thickness even if it can be produced, but it seems interesting to try to investigate within this range.

For each sample Tc has been measured by an inductance method. It was thus possible to see in what ways the hot press processing is affecting the Tc.

---

* Here \( \lambda \) is the London penetration depth and \( K = \lambda/\xi \) where \( \xi \) is the coherence length - \( \lambda \approx 2500 \) Å, \( \xi \approx 50 \) Å according to RCA Reviews (Ref. 19). These two parameters are temperature dependent through the expression \( (1 - T/T_c) \) which is always close to 1 since \( T = 4.2^\circ K \) (liquid helium temperature) and \( T_c \) from 12° to 18°. The correction we could bring here would be small compared to the inaccuracy in \( \lambda \) and \( \xi \) measurements.
II. HOT-PRESS PROCESSING

The powder consisting of commercially available -400 mesh Nb, -400 mesh Sn and spectrographic graphite was carefully mixed for 24 hours in a rolling mill. The mixture was then put into a graphite die, pressed at 8,000 psi and heated by a tantalum filament surrounding the die.

During all the heating the gas pressure was kept under 300 mm of mercury. An increase of pressure due to out-gassing and vaporization of the tin occurred at the beginning of each run.

The temperature was read every two minutes through a window by an optical pyrometer. The top of the main graphite die was chosen as a reference for temperature measurements.

At the end of the sintering the current was cut and argon was admitted into the chamber at a pressure slightly lower than the atmosphere pressure to cool down the sample.

The sample, in the form of 10x3x3 mm "parallelipiped" was then taken out and tested as we will see later on.
III. STRUCTURE

A. General Features of the Structure

Sample micrographs can be seen. Two kinds of etching solution were used: a) 50% lactic acid, 40% nitric acid, 10% hydrofluoric acid. This solution reveals the NbC structure but does not etch Nb$_3$Sn; b) 10 ml of saturated chromic acid and 1 g of sodium fluoride. It is then possible to see the structure of the continuous phase which is, according to x-rays and microprobe work mainly Nb$_3$Sn. (See plates 14, 15).

We have a continuous evolution from the NbC "islands" in a Nb$_3$Sn "sea" (high tin content, relatively low sintering temperature), see plate 2, to the NbC "matrix" with Nb$_3$Sn in the grain boundary, see plate 3, (small tin content, high sintering temperature). The NbC grain size is the same as the size of the Nb powder we started with: around 40μ for the largest grains or powder particles.

Twins are frequent in the fcc NbC and might indicate some thermal strain during cooling due to the fact that NbC and Nb$_3$Sn may have different thermal expansion coefficients.

The Nb, Sn, C powder mixture probably starts reacting around 900°C when the reaction 3Nb + Sn → Nb$_3$Sn takes place at an appreciable rate. The formation by a diffusion process of stoichiometric NbC is very slow. All x-ray diffraction patterns yield a smaller parameter than pure NbC. This parameter corresponds to a composition in between C/Nb = 0.76 and C/Nb = 0.66. The carbon content in NbC decreases with the temperature and the length of time of the sintering.

One can see as illustrated by plates 4,5,6 a variation of the structure from the surface to the bulk of the sample. Nb$_3$Sn grain boundaries are thinner near the surface and as shown by x-rays when we examine a section
near the surface the NbC lattice parameter is larger and corresponds in one case to a composition of .83 C atoms for 1 Nb atom. This feature is likely due to the graphite diffusion from the graphite die.

According to Giorgi and coworkers NbC can never be a superconductor within that composition range.7

B. Influence of the Hot-Press Processing Upon the Structure

Two kinds of heat treatment were carried out:

1) Raising of the temperature to a plateau from 1500°C to 2150°C, in 4 to 6 minutes and staying here for 4 minutes to 60 minutes, then cooling with argon.

ii) Same beginning procedure but with a second plateau at a lower temperature and still cooling with argon. Four samples have been treated in this manner. Table I gives all the information concerning heat treatment, composition and \( T_c \) results.

The equipment did not allow us to run safely at a temperature higher than 2100°C.

From 430°C up to 900°C, Sn is liquid and free. During the first one or two minutes of the sintering we can see an increase of pressure which is due to tin losses by evaporation. This cannot be due to out gassing only since the increase of pressure is much larger with this tin mixture than with other material whose vapor pressure is lower. The time duration of this first step is very important and the lack of control we have here can explain some difficulties we have in reproducing "identical" samples. This discrepancy does not appear too much when we look at the structure but rather on the \( T_c \) or \( H_{c2} \) measurements. Up to now attempts to reproduce the best sample (4B) have been only partially successful.
Some general trends can be observed.

For the same composition the higher we get in temperature, the thinner is the $\text{Nb}_3\text{Sn}$ boundary. (See Plates 10-12).

A too short sintering time leads us to unreacted carbon and thus to a porous material. See Plates 16 and 17.

In two cases the second plateau in temperature (1300° - 1600°) produces a third phase which is $\text{Nb}_2\text{C}$ according to x-rays. (See Plate 13) This phase is surrounding the NbC phase and can be developed during the "annealing" of the $\text{Nb}_3\text{Sn}$ phase. Tin will diffuse to the surface and evaporate, the remaining Nb will then stay in place and C from the NbC phase will diffuse in Nb, thus giving $\text{Nb}_2\text{C}$. The number of Nb atoms per unit volume in the four phases $\text{Nb}_3\text{Sn}$, Nb, $\text{Nb}_2\text{C}$, and NbC is not much different (6.25, 8.60, 6.86 7.53 gm/cm$^3$) for the stoichiometric material so the diffusion process which is proposed would involve mainly Sn and C atoms.

C. Influence of Composition Upon the Structure

In some samples we can see some heterogeneity. (See Plate 7) This can be due to the heterogeneity of the initial powder. The graphite powder which is much thinner and much lighter than the Nb and Sn powder segregate and even a 24-hour period in the rolling mill is not a very satisfactory mixing process.

An excess of graphite*(Sample 9) causes some pores which are due to unreacted graphite taken away by polishing. The type 9 samples are very porous. They have been generally overlooked because of their

*By excess of graphite we mean the excess of graphite that still exists after the following reactions: (I) $3\text{Nb}+\text{Sn(left)} \rightarrow \text{Nb}_3\text{Sn}$, (II) $\text{Nb}$ (after I) + 0.7C $\rightarrow \text{Nb}_1\text{C}_0.7$. 0.7 C for 1 Nb seems to be the average NbC composition for the treatment involved.
porous aspect but it will be interesting to test their critical current-critical (field) performances. The porosity according to Hancox,\textsuperscript{10} can provide a better thermal capacity by allowing liquid helium to enter the material, thus may lead to a better upper critical field $H_{c2}$ by taking away Joules heating which might increase the temperature of the sample to a value higher than 4.2°K.

The initial tin content does not seem to matter very much. Yet if it is high, as in the case of the type 2 sample, we get the "island" configuration (see Plates 14 and 15) with a continuous sea of Nb$_3$Sn if the temperature of sintering is low enough. If it is small, as in the case of the type 8 sample, (see Plates 3, 7-9), we get the matrix configuration. As pointed out before, the time during which Sn is free seems to be very important. Furthermore the temperature and the duration of the sintering are affecting the Nb$_3$Sn phase proportions both in the same way.
IV. CRITICAL TEMPERATURE RESULTS

$T_c$ was recorded by inductance measurement. A coil in which a small AC current was sent at 80 cycles/sec was surrounding the sample. The whole apparatus was plunged slowly into a liquid helium dewar. The temperature gradient allowed us to measure accurately the superconducting transition, that is to say the flux exclusion and thus the voltage drop in the coil. The temperatures were recorded by a calibrated germanium semiconductor. Two measurements were systematically taken: one going down (decrease of temperature) and one going up (increase of temperature). The results are recorded in Table I.

The three important results are the following:

As the temperature of sintering increases, $T_c$ and $\Delta T_c^*$ decreases.

The second plateau of the sintering process improves $T_c$ but does not seem to affect $\Delta T_c$ very much.

Some articles in the literature have discussed Nb$_3$Sn critical temperature and have offered some interpretations.\textsuperscript{11,12} This seems to be a difficult problem. An agreement seems to have been reached that there is a strong correlation between $T_c$ and the probability of the existence of a continuous niobium chain in the $\beta$ tungsten structure.

A large $\Delta T_c$ is attributed to inhomogeneity in stoichiometry.

The scope of this work does not allow us to use these conclusions but one can expect high sintering temperatures to lead to compositions away from stoichiometry and thus a small $T_c$, and to inhomogeneities in stoichiometry, resulting in large $\Delta T_c$.

There seems to be a contradiction between high $T_c$ and thin boundaries which are both expected to yield good $H_{c2}$ performance: thin boundaries

\[ \Delta T_c^* = T_{ INITIAL} - T_{FINAL} \]

of the superconductive transition.
are to be obtained by high sintering temperatures which lead to small $T_c$. The solution would be to make a sintering at high temperature and then "anneal" to improve $T_c$. This is the purpose of the second plateau in the sintering process.

However, as we will see later the thicknesses we have to get to have a "thin film" effect are much smaller than what we are able to obtain: 250Å - compared to 5000Å or maybe even 1000Å. Furthermore $T_c$ does not seem to be a parameter of paramount importance for high field purpose at least within a certain "quality range". The structure of the superconducting phase, impurities, scattering centers, dislocations, and stresses could be more effective than $T_c$. 6
V. CRITICAL CURRENT DENSITY. CRITICAL FIELD RESULTS

A. Experimental Set Up

Four samples have been tested in a pulsed magnetic field. The samples were cut with a spark cutter down to a cross section of about 1 mm$^2$. Both ends were cover plated with copper by electrodeposition in a solution of NaCN-NaOH, Na$_2$CO$_3$ and CuCN and then soldered onto a standard four wire probe. The tests were made in liquid helium, H being perpendicular to J.

Voltage contacts were from 1 cm to 0.6 cm apart. The intensity of the calibrated pulse (6 millisecond) and the voltage across the sample were recorded on the screen of a two beam oscilloscope. Pictures of the traces were taken with a high speed Polaroid film. For a given field two pictures were taken, with and without current, in order to subtract the voltage induced by the up surge of the field in the sample circuit (see Ref. 19). Plate 1A shows a typical picture and Plate 1B explains the way we deduced the resistive critical field $H_r$, beginning of the resistive transition and the critical field $H_{c2}$, end of the superconducting state.

We met two limitations in this test: The upper pulse peak we could get without damaging the equipment was 205 kG and the current had to be kept above 1 amp because of noise problems.

One of the samples, 4B, displayed a high current density at high field (203 kG). The current density was 5000 A/cm$^2$ if we assume (and this seems conservative) that 1/10 of the area is made of the Nb$_3$Sn phase.

If we extrapolate the curve as $J$ goes toward zero, we get 240 kG which is better than any previously reported value (See Fig. 1).
B. Theoretical Formulation

Our initial idea was to attempt to get very thin grain boundaries and hence to improve the critical limit of \( H_{c2} \).\(^{13-15}\) Let us review some of the most important theoretical work.

1. Bulk Sample

According to Ginzburg, the upper critical field derived from the GLAG theory (in the case of a bulk material) can be written:

\[
H_{c2} = 2 \sqrt{2} K H_c / [1 + (t)^2]
\]

with

\[
K = K_0 + 7.33 \times 10^3 \rho_n \gamma^{1/2}
\]

\( K_0 \) being a dimensionless constant dependent upon \( T_c \), \( \gamma \), \( \rho_n \) and \( S_f/S \)

\[
K_0 = 1.61 \times 10^{24} (T_c \gamma^{3/2}/n^{1/3}) (S_f/S)^2
\]

and

\[
H_c = 2.42 \gamma^{1/2} T_c (1-t^2) \quad H_c: \text{thermodynamical magnetic field}
\]

with

\( t = T/T_c \) reduced critical temperature

\( \rho_n = \text{normal resistivity} \)

\( \gamma = \text{electronic specific heat} \)

\( n = \text{number of "valence" electrons per unit volume} \)

\( S = \text{free area of the Fermi surface} \)

\( S_f = \text{free area of the Fermi surface for a free electron gas of density} \ n. \)

Finally, we can write

\[
H_{c2} = 2 \sqrt{2} (K_0 + 7.33 \times 10^3 \rho_n \gamma^{1/2}) 2.42 \gamma^{1/2} T_c (1-t^2/1+t^2)
\]

\[
H_{c2} = C (K_0 + C' \rho_n \gamma^{1/2} T_c (1-t^2/1+t^2)
\]

\[
H_{c2} = C (C' T_c \gamma + C'' \rho_n) \gamma T_c (1-t^2/1+t^2) \quad C, C' \text{ and } C'' \text{ being constant}
\]
The BCS theory leads to the fundamental equation

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

where \( V \) = interaction potential between paired electrons

\( N = \) the density of state for electrons at the Fermi surface

Unfortunately \( V \) is generally unknown.

From formulas 1) and 2) we can see in which ways we have to work to improve \( H_{c2}(T) \). This has to be done through \( T_c \), \( \gamma \), and \( \rho_n \) which have to be independently the highest possible.

It should be emphasized that these relations have been established by physicists who are dealing with very simple models. It is therefore hazardous to extend them to the metallurgical problems in a straightforward way.

In the case of a bulk upper critical field limit, theoretical limits have been set. The Clogston limit\(^{16}\) which has been established considering the Pauli paramagnetic free energy of the normal state as a minimum leads to the formula:

\[ H_{c2} \leq H_p = 1.84 \times 10^4 T_c \left( 1 - \left( \frac{T}{T_c} \right)^2 \right) \]

which will lead for ideal \( \text{Nb}_3\text{Sn} \), at 4.2°K, to 320 kG.

A recent article\(^{17}\) is more optimistic since the theoretical limit for \( H_{c2} \) at 4.2°K would be 880 \times \( \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right] = 835 \text{ kG} \). In any case there seems to be room enough for improvements since the best \( \text{Nb}_3\text{Sn} \) known until now had an extrapolated resistive field, \( H_r(J = 0) \), of 214 kG only,\(^{18}\) and since a fair extrapolation led us to \( H_{c2}(J = 0) = 240 \text{ kG} \) in one case. (See Fig. 1.)
2. Thin Film Properties

In the case of a thin film specimen the picture is less complete. As the film thickness is decreased, the increase of $H_{c2}$ above the bulk material value becomes significant in the vicinity of a critical thickness $d_c$ which can be written according to Berlincourt,\textsuperscript{15} as

$$d_c = 2\sqrt{5} \lambda/\kappa(t)$$

with

$$\kappa = \lambda/\xi$$

taking

$$\lambda = 2500\text{Å} \text{ and } \xi = 45\text{Å} \quad (\text{ref 19})$$

This yields to

$$d_c \approx 250\text{Å}$$

As we have seen above $\lambda$ and $\xi$ are temperature dependent but their variations are small compared to the inaccuracy in the measurement, and then for very thin films

$$H_{c2}(d-250\text{Å})/H_{c2}(\text{bulk}) = 2\sqrt{6} \lambda/d.$$ 

So far we have been able to get down to 5000Å and in some cases 1000Å which is still an order of magnitude too high to obtain this film effect.

C. Results

The critical current-critical curves are plotted in Figs. 1 and 2. It would be difficult and hazardous to draw any definitive conclusions from these four tests only. The good performance of specimen 4B cannot be explained by a thickness effect since the grain boundary is in the thinner regions, $1\mu = 10,000\text{Å}$ wide, that is to say 40 times too large. So far we did not see any thickness effect. As a consequence the microstructure of the superconductive phase through $\rho_n$ and $\gamma$ seems to play the only role. $T_c$ is not a good parameter to look for by itself since we do not observe any correlations between $H_{c2}$ and $T_c$ for the
four samples. This means that $\gamma$ and more likely $\rho_n$ are to be taken into account. More data are needed to come up with a conclusion.

The very complicated configuration of the superconducting phase may allow some grain boundary path to be continuously parallel to the external field. The good results we obtained for the sample 4B (and this remark is true for all the samples) might be due to the fact that we are not measuring $H_{c2}$, but in fact $H_{c3} = 1.695 H_{c2}$ (ref. 13) according to St. James and De Gennes. However, whether this sheath superconductivity is able to carry a large current (here 5000 amp/cm$^2$) or not is a question which is still to be answered. Besides the sheath superconductivity would disappear at fields lower than $H_{c3} = 1.695 H_{c2}$ when the surface of the superconductor is clad with another normal phase which is the case here (proximity effect). Moreover this sheath conductivity is to occur only when the interface superconductor-normal material is very smooth (when the local irregularities are larger than the coherence range distance $\xi = 45\text{Å}$). It seems difficult in the scope of this work to decide whether or not this sheath superconductivity should be taken into account.
VI. CONCLUSIONS

It has been possible in this work to control by hot press processing and composition of the powder the thickness of the Nb$_3$Sn superconducting phase in the grain boundary. However the thinnest grain boundary we obtained (1000Å) is still too thick to fall in the range of the critical thickness (250Å) which is thought to improve the upper critical field $H_{c2}$ like $\lambda/d$.

The critical temperature of the sample can be, to a certain extent, correlated to the temperature of the sintering and an annealing can increase it.

The data we have for the critical current-critical field measurement are insufficient to draw any definitive conclusions. However, we have found in one case a high extrapolated upper critical field, 240 kG at 4.2°K.

In many applications (magnet, transport of current, transformer) which would involve the use of a superconductor$^{21,22}$ only $H_r$, the beginning of the resistive transition is relevant. $H_r$ is generally the field value which is studied in the literature (Kim-Anderson theory$^{23,24}$). Whether $H_r$ and $H_{c2}$ are going to the same limit when the current goes toward zero is not yet really known. It is therefore questionable to compare our results for the extrapolation of $H_{c2}$ (as $J$ goes toward zero) and some other established results in the literature which are concerned with the limit of $H_r$,$^{18}$ even then if in one of our samples $H_r$ and $H_{c2}$ seem to have the same limit.*

The number of parameters involved, composition of the powder, and hot press processing was such that this work can only be considered as an exploratory work. It should be emphasized here that our best sample

*In the three other samples the determination of $H_r$ was not accurate enough to allow us to draw $J$ versus $H_r$ curve.
was to a certain extent picked at random among a choice of about 10 samples only. Further work will be necessary to investigate the $H_{c2}$ and $J$ dependence upon structural parameters (dislocations, precipitates). It will be interesting to investigate the Nb$_3$Sn grains boundary through electron-microscopy. R. Silverman$^{20}$ has given a carbon replica method.

It will be interesting too to start the sintering with smaller powder. Since the NbC grain has the same dimensions as the Nb grain powder and since the dimensions of the grain boundaries are likely to be the same, in the same condition, the sintered material will then have more superconducting paths and then be able to carry more current. This is a way to cut down the noise of the voltage signal by operating at higher current intensity.

The brittleness of these "NbC, Nb$_3$Sn," "matrix" superconductors leads us to doubt their potential engineering applications. However, the $\beta$ tungsten structure is not confined to Nb$_3$Sn and C is probably not the only third element leading to such a structure. New investigations are being undertaken to prospect this field.

A new pulsed field equipment is to be built. It will be possible to investigate up to higher field (300 kG). Any extrapolation is hazardous in this area because we do not have many examples to rely on. If we follow the theoreticians$^{17}$ Nb$_3$Sn, in a bulk form only, would lead to $H_{c2}(0) = 880$ kG. From 214 kG (extrapolated from Montgomery's results) or 240 kG (our best extrapolated result) to 880 kG, there is still plenty of room left and a long way to go.
ACKNOWLEDGEMENTS

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<table>
<thead>
<tr>
<th>Denomination</th>
<th>Samples</th>
<th>Composition</th>
<th>Hot press processing</th>
<th>( T_c ) results</th>
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<td>11.4 3.9</td>
<td>* Here 5.4 is the beginning of the transition (5.4)* ?</td>
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<td>12.6 1.4</td>
<td>1 Second plateau at 1350°C for 25 min.</td>
</tr>
<tr>
<td>2E</td>
<td>-</td>
<td>-</td>
<td>2000+ 25</td>
<td>12.7 3.5</td>
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</tr>
<tr>
<td>10A</td>
<td>1</td>
<td>0.4 0.1</td>
<td>1450 4</td>
<td>17.8 0.2</td>
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</tr>
<tr>
<td>10B</td>
<td></td>
<td></td>
<td>2000 21</td>
<td>14 2</td>
<td></td>
</tr>
<tr>
<td>10D</td>
<td></td>
<td></td>
<td>2130* 20</td>
<td>No transition visible</td>
<td>*Second plateau at 1000°C for 10 min.</td>
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<tr>
<td>8B</td>
<td>1</td>
<td>0.5 0.1</td>
<td>1800 20</td>
<td>14.9 2.7</td>
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</tr>
<tr>
<td>8A</td>
<td></td>
<td></td>
<td>2150 24</td>
<td>13.9 2.4</td>
<td></td>
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<tr>
<td>8C</td>
<td></td>
<td></td>
<td>2050+ 20</td>
<td>16.7 2.2</td>
<td>* Second plateau at 1350°C for 20 min.</td>
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Table I
### Table I (continued)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Composition</th>
<th>Hot press processing</th>
<th>$T_c$ results</th>
<th>Remarks</th>
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<tr>
<td></td>
<td>Denomination</td>
<td>Nb</td>
<td>C</td>
<td>Sn</td>
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<tr>
<td>6</td>
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<td>1</td>
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<tr>
<td>9</td>
<td></td>
<td>1</td>
<td>0.8</td>
<td>0.1</td>
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</tbody>
</table>

---

*Composition: for 1 atom Nb, $x$ atom C, $y$ atoms Sn*

*T$_c$ was taken as the middle of the transition and has been investigated for $T > 4.2\,^\circ$K only*

*$\Delta T_c = T_{\text{initial}} - T_{\text{final}}$
SAMPLE 4B
H \perp J
T = 4.2^\circ K

- \triangle H_r RESISTIVE CRITICAL FIELD
- \triangle H_{C2} UPPER CRITICAL FIELD
- \dagger TRANSITION NOT COMPLETED

CURRENT DENSITY, Amp/cm^2

CRITICAL FIELDS, Kilogauss

0 50 100 150 200 250

0 5000 10000 15000 20000 25000
$H \perp J$
$T = 4.2^\circ K$

**SAMPLE**

- △ 4B
- □ 7A
- ▼ 8'C
- ◇ 8''C
- ○ 10B
- ↓ TRANSITION NOT COMPLETED

**CURRENT DENSITY, Amp/cm²**

**$H_{C2}$ UPPER CRITICAL FIELD, Kilogauss**
Plate 1A

\[ H_r: \text{ Beginning of the Resistive Transition.} \]

\[ H_{c2}: \text{ End of the Resistive Transition (Normal Resistivity) and end of the Superconductive Mixed Stage.} \]

Plate 1B
The Two Types of Structure

Plate 2. Sample 8B ×250. "Island" type. The sintering temperature was only 1300°C for 20 minutes.

Plate 3. Sample 8A ×250. "Matrix" type. Same composition of the powder as above but the sintering temperature is much higher. 2150°C for 24 minutes.
Plate 4. Sample 10B. X1500. Decrease of the grain boundary thickness around a grain due to the proximity of the surface (below).
Plate 5. Sample 10B. X600. Bulk part.

Plate 6. Sample 10B. X600. Surface proximity (left).

This type of heterogeneity can explain the difference we have found in the case of sample 8, critical field-critical current measurement. For example, see Fig. 2 in the case of sample 8°C and 8"C.
The Two Types of Bulk Structure (Island and Matrix) in the Sample

Plate 7. Sample 8B. ×500. This happens when the sintering temperature is in an intermediate range. From 1800°C to 2000°C. Here T = 1800°C.
Plate 8. Sample 8B. \( \times 1000 \). Thin boundaries (matrix type).

Plate 9. Sample 8B. \( \times 1000 \). Island type.
Thin Grain Boundaries

Plate 10. Sample 10B. X1000. Thickness ~1μ.

Plate 11. Sample 8A. X2500. Thickness ~0.5μ.
Plate 12. Sample 8A. X1500. Thickness 0.1µ.
Plate 13. Sample 2E. X250. The round grains surrounding NbC grain are Nb$_2$C grains.
Etching of the Superconducting Phase

Plate 14. Sample 2C. X500

Plate 15. Sample 2C. X1000.
Low Temperature Structure.


Plate 17. Sample 7. X1000.
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