METALLURGY OF CONTINUOUS FILAMENTARY A15 SUPERCONDUCTORS

by

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I. Introduction

Composite superconductors, which consist of fine filaments of superconductors in normal metals, have gained almost universal acceptance in magnet construction. These composites are usually twisted in order to increase their electromagnetic stability and reduce the energy loss in time-varying magnetic field applications. Originally the superconducting materials used in these composites were restricted to the ductile superconducting alloys, mainly Nb-Ti. However, owing to a need for improvements in the design of magnets for superconducting synchrotrons and for magnetic fusion reactors, metallurgical methods for producing such filamentary conductors with brittle Al5 structured superconductors were developed in the past few years. In 1969-1970, a method for fabricating such conductors with Nb3Sn and V3Ga was successfully developed and is now called the bronze process. The method relies on the fact that these Al5 compounds can be formed at the interface of Nb(V) and Cu-Sn(Ga) when such composites are heated at elevated temperatures.

Since the discovery of the "bronze process", many small-scale magnets have been successfully fabricated. Large-scale applications of these materials to magnets for magnetic fusion reactors and high-energy accelerators are being designed and tested. Also the manufacturing technology for these composites have been developed to the extent that fabrication of large quantities of these wires is now possible. Thus, it seems desirable to recapitulate the early history of the "bronze process" and to describe modifications to the process which have since followed. The metallurgical principles, which are involved in the process, are described including the kinetics of the compound growth, the effects of additives on the growth, etc. The superconducting
properties of these compounds are also discussed. In particular, the influence of metallurgical variables on the superconducting properties is discussed in detail. In discussing the superconducting current densities in these compounds, limits in applicability of existing magnetic-flux-pinning models are also treated as well as methods for determining critical magnetic fields. Earlier reviews on this subject were also presented by T. S. Luhman and J. D. Livingston.8

II. History of the "Bronze Process"

A. Early History

Perhaps one of the most intriguing aspects related to the discovery of the "bronze process" is that the discovery was independently made by three metallurgists in three countries at approximately the same time. They are K. Tachikawa at the National Research Institute for Metals in Japan, A. R. Kaufman at the Whittaker Corp. in the USA, and E. W. Howlett at the Atomic Energy Research Establishment at Harwell in Great Britain. The work by Howlett is little known to the community of the people working on multifilamentary Al5 superconductors. However, it is quite clear that he has been working on the "bronze process" and that he filed a claim for a British Patent in October 27, 1959. I have been told that Howlett was lost in an accident in the mountains soon after his discovery of the process. This is probably the reason for not hearing about his contribution to the technology of fabricating Al5 multifilamentary superconductors.

In the USA, W. B. Sampson, who had been developing superconducting dipoles for high-energy accelerators, realized the potential benefits which might be achieved with Nb3Sn multifilamentary wires over the available Nb-Ti wires for his applications. In 1968 he approached David H. Gurinsky, who was the Division Head of the Metallurgy and Materials Science Division at Brookhaven National Laboratory, asking him to develop methods for fabricating fine
multifilamentary wires with brittle A15 compounds such as Nb$_3$Sn. Gurinsky, in addition to introductory work with M. Garber and A. McInturff, visited his old friend A. R. Kaufman at Nuclear Materials Division of Whittaker Corp. to obtain his advice and help on this problem. Kaufman suggested the idea of the use of Nb rods in a Cu-Sn alloy and then reacting to form Nb$_3$Sn layers after the necessary reduction in size required to obtain the filaments of Nb in the Cu-Sn matrix. This is schematically illustrated in Fig. 1a. This idea was successfully carried out by J. J. Pickett immediately following the Gurinsky-Garber visit. The result was first reported at the Applied Superconductivity Conference at Boulder, Colorado in 1970 by A. R. Kaufman.\(^2\)

Meanwhile, Tachikawa, who had been studying the preparation of V$_3$Ga tapes in Japan, also realized that V$_3$Ga could be formed by a solid-state reaction at the interface between V and (Cu-Ga) and the produced V$_3$Ga tapes by this method. This result was first reported at the International Cryogenic Engineering Conference in Berlin in 1970 also. The following are studies which he and his co-workers performed which led him to the discovery of the process.

Research on superconducting materials at the National Research Institute for Metals was initiated by K. Tachikawa in 1962. At first he and his co-workers studied Nb-Zr and Nb-Ti alloy systems, and then they concentrated their efforts on investigation of A15 superconductors, primarily V$_3$Ga tapes. One of their early contributions to the fabrication of A15 conductors was to produce a V$_3$Ga tape by a liquid diffusion process which carried very high current at high magnetic fields.\(^10\)

When vanadium, V, is reacted with liquid gallium, Ga, below 500°C, the dominant phases, which form at the interface, are nonsuperconducting VGa$_2$. 
and $V_3Ga_2$. Only a small amount of the superconducting phase, $V_3Ga$, is formed along grain boundaries in the $V$ substrate next to $VGa_2$ as schematically shown in Fig. 2a. It was noted that the Al5 phase would grow significantly if a small amount of Cu was plated on the outside surfaces of the tape. It was also observed that the addition of Cu not only increased the thickness of the $V_3Ga$ layer at the expense of $V_2Ga$ and $V_3Ga_2$, but also made the growth of the $V_3Ga$ layer to be very uniform in thickness as shown in Fig. 2b. Furthermore, the resultant $V_3Ga$ layer contained only a very small amount of Cu (less than 1 at.%). Noting that the Cu acted as a catalytic agent for the preferential growth of the $V_3Ga$ phase, Tachikawa, presumably, extended this idea successfully to the formation of the single-phase $V_3Ga$ at the interface of $V$ and a Cu-Ga alloy. The superconducting properties of $V_3Ga$ tapes, which were produced by this technique, were then reported at the International Cryogenic Engineering Conference at Berlin. About this time and without the knowledge of his work, the first multifilamentary $V_3Ga$ was fabricated by Suenaga and Sampson at BNL. This work on $V_3Ga$ and Kaufman's report on $Nb_3Sn$ led to the opening of a gate for a flood of investigations in this very interesting and technologically important area of superconducting materials all over the world in the ensuing years.

B. Evolution of the Process

Since the original discovery of the "bronz process", a number of modifications have been introduced in order to improve or reduce some of the difficulties inherent in the process. In this section, all of these modified fabrication methods are described and evaluated with respect to their uses on the large-scale production of these wires.

1. **The Ta Diffusion Barrier** - Before various modifications for the "bronz process" are discussed, a very important contribution by the Harwell group
in the development of multifilamentary Al5 wires has to be mentioned. This is the use of Ta as a barrier for Sn diffusion to the Cu stabilizer from the bronze matrix. As mentioned earlier, there are two requirements for the stabilization of superconducting wires: 1) fine twisted filaments and 2) high-conductivity Cu adjacent to superconductors. Since the "bronze process" necessitates the presence of a high-resistivity matrix next to the superconducting filaments, it is desirable to place high-purity Cu as close to the filaments as possible; the Sn in the bronze must be prevented from contaminating the Cu. Thus, this concept of a Ta diffusion barrier has made practical use of multifilamentary Al5 wires possible by making inclusions of high-purity Cu as a part of the wire in an economical process. Also, it is now possible to use Nb foils which are locally doped with P instead of Ta for the diffusion barrier. One of the ways to achieve this is to ion-implant the niobium with phosphorus P, but this appears to be too costly for commercial applications. It was found that the simplest way was to sheath the niobium in a commercial phosphorus-bronze choosing the thickness of the sheath as a compromise between outward diffusion of P affecting adjacent filament reaction and keeping the concentration of P adjacent to the barrier sufficient to inhibit reaction.

2. The External Diffusion Process - The first modification, the external diffusion process, to the "bronze process" was introduced by Suenaga and Sampson soon after the discovery of the original "bronze process" following a suggestion to increase thickness of the layer in the bronze-processed V$_3$Ga by Ga-plating the wire. (Again, it is interesting to note that W. Fietz and R. Scanlan at the Intermagnetics General Corp. and the General Electric Co., respectively, were also in the process of developing the external diffusion method for fabrication of Nb$_3$Sn multifilamentary wires without being aware of the work at BNL.) This process consists of extruding a Nb-Cu composite and drawing it to a final size; e.g., 300 um. Then, the wire was coated with a
a layer of tin before heating it to make a Cu-Sn alloy matrix and then Nb$_3$Sn filaments. This process is schematically illustrated in Fig. 1b. The main advantage in this process over the original one is that a Nb-Cu composite can be drawn to a small size without any intermediate annealing while Nb-(Cu-Sn) or V-(Cu-Ga) composites require frequent annealing steps to remove work hardening of the matrix. In this process, new problems have been encountered in the tin-plating process and subsequent heat treatments to diffuse the tin into the Cu matrix to form a Cu-Sn alloy and Nb$_3$Sn filaments. The primary difficulty is delamination of the outer layer of the wire when the plated Sn layer was greater than \( \sim 5 \) \( \mu \)m. Thus, the maximum wire size for this process was limited to \( \sim 0.25 \) mm in diameter because a thicker Sn layer is required for complete reaction of Nb to Nb$_3$Sn for larger wires. This problem is thought to be caused by the volume expansion of the outer layer by diffusion of Sn in the Cu matrix and by the Kirkendal voids. Some progress has been made in controlling the delamination by modifying the Sn plating and heat-treating methods. Wires made by this method do not contain the gross delamination, although small irregularities at the surface are still observable in these wires.

Recently, a new approach was suggested to eliminate these voids and thus the delamination. This consists of an annealing step at \( \sim 500 \) to 750°C of the (Nb-Cu) composite before tin plating and heat treating to diffuse the Sn. It is believed that this step eliminates heterogenous nucleation sites for void formation. However, this additional heat-treating step cannot significantly increase the size of the wire to be employed for the "external-diffusion" process without introducing the delamination problem or other difficulties such as "beading" of Sn.

An additional benefit of this process is that the concentration of Sn in the matrix is not limited to \( \sim 13 \) wt% as in the case of the "bronze process".
A high Sn concentration in the matrix normally results in a high critical-current density for Nb₃Sn layers. Thus, it is likely that the $J_c$ of wire made by this process will be higher than that for the wire made by the "bronze process". Another advantage in this process is that a third elemental addition to the matrix such as Ga to improve superconducting properties is possible without reduction in the Sn content of the Cu-Sn alloy since this addition can be made after the Sn-diffusion process is completed when no further mechanical reduction is required.

Although this new process has eliminated one of the major drawbacks of the "bronze process", and it can produce wires with higher $J_c$ than in those by the "bronze process", and some further progress has been made toward coping with the delamination of the outer matrix layer during the Sn-diffusion process, its use for production of conductors for large magnets is expected to be limited to certain types of conductor configurations. This arises because it cannot be used with the Ta-diffusion barrier and the Cu stabilizer at the outside portion of a wire. However, in some conductors such as braided cables, this limitation may not be a major problem since wires for stabilization can be braided in the cable with the superconducting wires. In this case, the Cu wires have to be protected from Sn diffusion by having the Ta barrier at the outside of the wires. Also, the braids normally require relatively small wires (~30 μm). Thus, the limited maximum wire size in this process will not be a disadvantage. However, in some other cables or conductor designs, it is expected that there will be cases where a larger wire size would be desirable.

3. The Internal Tin Diffusion Process - In 1974, a new modification to the bronze process was reported by Hashimoto et al. This process consists of assembling Cu-clad Nb-bars and a Cu-clad (Sn-20 at.% Cu) alloy* rod was shown later that a pure Sn rod can also be used for this purpose.
in a Cu tubing such that the (Sn–Cu) rod will be at the center; the assembly is then cold drawn to final size for heat treatment to form the Nb$_3$Sn (see Fig. 3a). As in the case of the external-diffusion process, the main advantage of this process over the "bronze process" is the elimination of the intermediate annealing steps in the "bronze process". In addition, this has an advantage over the external-diffusion process in that the Cu stabilizer and the Ta barrier can be placed outside a wire since Sn is contained at the center of the wire. The Sn concentration in the matrix will, however, be limited and will not be as high as that for the external-diffusion process. One possible difficulty with this process is that in large-scale applications the length of a wire which can be fabricated by this method is limited since the billet assembly cannot be extruded without melting the Sn–Cu alloy.

4. **Bronze in Nb Tubing** - In 1975, two similar modifications to the "bronze process" were proposed. Both of these employ Nb tubing instead of rods. In one case, Cu–Sn alloy rods are inserted in Nb tubes which are encased by Cu (see Fig. 3b). A number of these units are assembled inside a Cu tube for extrusion and wire drawing. In the second case, a Sn–Cu alloy or Sn rod is inserted in a Cu tube which is in turn placed in a Cu-encased Nb-tube. A number of these basic units are stacked in a Cu tube for cold drawing to the final size and for heat treatment and formation of Nb$_3$Sn (see Fig. 3c). The common advantage in these processes over the "bronze process" is that the Nb tube acts as a diffusion barrier for Sn, thus the Ta barrier is not necessary. Furthermore, all of the Nb$_3$Sn layers will be very close to the Cu stabilizer while it is not always so for the other processes. Although the use of the tubing is not convenient, it was shown that a wrapped foil of a Nb foil around a Cu–Sn rod is sufficient for this purpose. On the other hand, the common disadvantage in these processes is that the minimum filament size
in these processes tends to be significantly larger than those wires by the bronze process. The larger filament size can lead to higher ac losses when these wires are placed in time-varying fields.

Although it has been shown that large conductors \((7.6 \times 7.6 \text{ mm}^2)\) and a large enough quantity of wire to make test coils can be fabricated by these processes, there still is a difficulty inherent in these processes. These methods of fabrication produce an internal stress resulting from the differential thermal contraction between \((\text{Nb, Nb}_3\text{Sn})\) and the matrix. Although the ratio of the bronze-to-the core \((\text{Nb}+\text{Nb}_3\text{Sn})\) is quite small (less than 1) producing a small longitudinal compressive strain on the \(\text{Nb}_3\text{Sn}\) layer, it turns out that a large radial tensile strain exists due to the contraction of the bronze at the core area. This strain reduces \(T_c\) and \(J_c\) in these wires. Especially, at very high magnetic fields, the reduction of \(J_c\) could be as large as an order of magnitude.

5. **WRAP Process** - As discussed above, these modifications to the original "bronze process" introduced some advantageous aspects in the fabrication of the multifilamentary Al5 compound wires, but all of these also introduced other difficulties. Recently, a new process was proposed which appears to incorporate some good features of the above modifications without introducing new complications. This process is schematically shown in Fig. 4; it consists of preparing a flattened Cu-Nb multifilamentary composite, wrapping this around a Sn-Cu alloy rod and cold drawing prior to the heat treatment to form \(\text{Nb}_3\text{Sn}\) filaments. Advantages of this fabrication method are that the intermediate annealing steps are eliminated and the length is limited only by the size of the Cu-Nb billets for extrusion. Furthermore, the Ta barrier and the Cu stabilizer can be wrapped over the composite after the wrapping process by similar techniques in a continuous manner. Another possible advantage is that some chemical elements, which could enhance
superconducting properties of the Nb$_3$Sn if added to the matrix, can be added to the Sn core without a significant reduction in the amount of Sn in the wire. For example, Be is known to improve the Nb$_3$Sn's mechanical property (the "strain tolerances" of the conductor$^{32}$) but its addition to the bronze matrix makes the wire very difficult to fabricate. A small amount of Be may effectively be added to the Sn core to improve this mechanical property.

This process is at an early stage of its development. At this time, it has been shown that the initial wrapping process can be performed on a commercial scale (see Fig. 4) and the wire can be drawn to a small diameter ($\approx 30$ μm) without any intermediate annealing steps (see Fig. 4). A preliminary measurement of superconducting properties was performed on this wire. The value of $J_c$ is comparable with those for the wires which were made by the bronze process. It should also be noted that this process may perhaps be more suitable for the in situ or similarly processed wires since in these wires the deformation of filaments during the flattening process will not be a problem.

6. Other Modifications - One of the most interesting approaches to fabrication of A15 filamentary conductors was proposed by C. C. Tsuei in 1973.$^{33,24}$ This process consists of casting a Nb-Cu melt to form a dendritic network of Nb in Cu, and of drawing this to wire. Sn can be added in the initial melt or added afterward before the heat treatment to form Nb$_3$Sn. An interesting aspect of this processing method is that the mechanical properties (yield strength and "the strain tolerances" of the wire) of this composite are greatly enhanced over the conventional multifilamentary Nb$_3$Sn or $V_3$Ga wires due to the close proximity of finely divided (<1000 Å) filaments. This process is now called the in-situ process. More recently, two modifications to the in-situ process were developed which use powder compacts of Nb and Cu powders. The approach extrudes the well-mixed and compacted Cu-Nb mixture essentially at room temperature$^{35}$ while the other extrudes it at an elevated temperature ($\approx 1000^\circ$C$^{36}$). After the extrusion process, Nb-Cu composites, which are very similar to the
in-situ processed wires, are produced and can be processed for \( \text{Nb}_3\text{Sn} \) formation as before by both of the methods. Since these subjects will be discussed in detail by R. Roberge, in this text, it will not be discussed further here.

III. Metallurgical Principles

Since the success of the bronze process for the growth of \( \text{A}15 \) compounds depends on the metallurgical processes taking place at the interface of two metals, (the so-called a diffusion couple), the formation and the kinetics of the growth of the compound layers at the interface are treated in detail in this section.

A. Thermodynamic Considerations

The formation of phases in a diffusion couple follows thermodynamic considerations. It is well established that the interfacial structures at a diffusion couple between two elements is composed exclusively of single phases appearing in the compositional sequence in which the corresponding phases appear according to the appropriate phase diagram.\(^{37}\) In multicomponent systems, the only phases which will form in these diffusion couples are those phases which lie on the most direct route, following the two-phase tie lines between two initial components of the couple.\(^ {38}\) The phases which most readily form are those with the most rapid kinetics of formation. In order to illustrate these points, we will first discuss a \( \text{Nb-Sn} \) diffusion couple and then compare the formation of phases in a \( \text{Nb-(Cu-Sn)} \), a \( \text{Nb-(Cu-Ge)} \), and a \( \text{V-(Cu-Si)} \) couple.

Commercial \( \text{Nb}_3\text{Sn} \) tapes have been produced for many years by heating \( \text{Nb} \) or (\( \text{Nb-1}\% \text{Zr} \)) tapes in a liquid tin bath. When these tapes are heated at temperatures above \( \sim 930^\circ \text{C} \), single-phase \( \text{Nb}_3\text{Sn} \) layers are formed. However, when they were heated at lower temperatures, the dominant compounds which
form at the interface are nonsuperconducting. The above difference in the
types of compound formation can be readily understood from the phase diagram
for the Nb-Sn system (Fig. 539). As it can be noted, the only stable phase
above 930°C is Nb₃Sn. However, at temperatures below 845°C, two other phases,
Nb₆Sn₃ and NbSn₂ are stable, and all three phases will grow at the interface
under proper conditions. The relative thickness of these compound layers are
primarily determined by the kinetics of growth. In this particular system,
The NbSn₂ phase is the most easily formed while the Nb₃Sn layer is the slowest
growth layer. However, if the composition of the mixture is 75 at.% Nb and
25 at.% Sn, the composite should eventually become totally Nb₃Sn since Nb₃Sn
is the most stable phase in this system (although the time scale for this to
happen will not be practical for most cases). As mentioned above, the termi-
nating phase is determined by the relative thermodynamic stability. As a
means to calculate the relative stability, the stability index, S.I. was in-
troduced by Raynor40 and is a convenient measure of the relative thermodynamic
stability of phases. The stability index for a compound AₓB₁₋ₓ\( (1-x) \) is defined as

\[
\text{S.I.} = T_m \left[ T_B + (T_A - T_B)(1-x_B) \right]^{-1}
\]

where \( T_m \), \( T_A \), and \( T_B \) are the melting temperatures for the compound, the ele-
ments A and B, respectively, and \( x_B \) is the atomic fraction of B in the com-
pound. This equation, in essence, indicates that those compounds for which
the melting point is above the line drawn between the melting temperatures for
the elements A and B are more stable than those with the temperature below it.
There exist other indices such as the formation temperature ratio (Hartsough41)
and the modified S.I. for the bronze process (Luhman et al.42) and these stabil-
ity indices can also provide insights into the relative stability of the phases.
The index developed by Luhman et al. can also give some indication of the effect
of the use of the bronze matrix on the relative phase stability in a binary
system.
For a better understanding the compound-formation processes in the "bronze process", appropriate ternary phase diagrams are required. Fortunately, portions of some of the relevant ternary diagrams have recently become available. We will consider three types of representative ternary phase diagrams: 1) (Nb-Cu-Sn), Fig. 6; 2) (Nb-Cu-Ge), Fig. 7; and 3) (V-Cu-Si), Fig. 8. It is now known that a single-phase A15 compound layer, multiphase nonsuperconducting compound layers, and an A15 phase and a nonsuperconducting phase layers are formed in these systems, respectively.

The first case (Nb-Cu-Sn) is an example in which the A15 phase is the only relevant stable phase, other than the terminal Nb (or V) and Cu-base solid solutions Cu-Sn (or Cu-Ga). Based on the work by Hopkins, Roland, and Daniels, Dew-Hughes constructed a part of a section of the Nb-Cu-Sn ternary phase diagrams at ~700°C, and this is shown in Fig. 6. This diagram shows that the diffusion path from the Cu-Sn solid solution to the Sn-Sn solid solution passes through only the A15 Nb3Sn phase field. Thus, this is the only phase which is formed at the interface of Nb and a Cu-Sn solid solution (or bronze). However, the shape of the A15 phase field in this diagram does not reflect some of the experimental observations: 1) Tc of Nb3Sn is always ~18 K regardless of the composition of the bronze, indicating the composition of Nb3Sn at the bronze interface is nearly 25 at.% Sn, and 2) the amount of Cu in Nb3Sn varies with the Sn concentration in the matrix. Since the shape of this phase field is very important in understanding the kinetics of the layer-growth, a schematic ternary section for this phase portion is proposed as shown in Fig. 9a to reflect these experimental observations. A similar section of the schematic ternary diagram for the V-Cu-Ga system is shown in Fig. 9b. The quantitative compositional analyses of V3Ga layers are not available from the literature. Thus, the A15 phase-field shape is meant to be illustrative qualitatively, based on my experience working with the system. It
should be noted that the compositional ranges in the single A15 phase for
$\text{Nb}_3\text{Sn}$ and $\text{V}_3\text{Ga}$ are significantly different. The maximum amount of Sn in
$\text{Nb}_3\text{Sn}$ is $\approx 25$ at.% while that of Ga in $\text{V}_3\text{Ga}$ is $\approx 30$ at.%. The difference in
the reaction temperature dependence of $T_c$ between $\text{Nb}_3\text{Sn}$ and $\text{V}_3\text{Ga}$ (see Section
III) may originate in this phase-field difference. However, without detailed
diagrams of this region of the $\text{V}_3\text{Ga}$ ternary diagram at several temperatures
the above possibility cannot be confirmed.

In the second ternary system (Nb-Cu-Ga), the most stable phase is
one in the Nb-Ge binary with a higher Ge content than the A15 phase. There
is no direct tie line to the A15 phase, and more importantly, as pointed out
by D. Dew-Hughes the A15 may not even lie on the direct tie-line route from
the most stable phase to the Nb-solid solution as shown in Fig. 7. In fact,
there appears to be two stable phases based on $\text{Nb}_3\text{Ge}_3$ and $\text{Nb}_3\text{Ge}_2$. Thus, the
superconducting A15 layer should not form during heating of a Nb-(Cu-Ge) couple.

In the third case (V-Cu-Si), both superconducting and nonsuperconducting
layers form simultaneously at the interface. The ternary section for such an
example is shown in Fig. 8. In this system two diffusion paths are possible as indicated. One from a low Si bronze (Si $< 1$ at.%) goes directly to
$\text{V}_3\text{Si}$; and the other, from the bronze with higher Si content, goes to $\text{V}_3\text{Si}$ via
$\text{V}_5\text{Si}_3$. Thus, $\text{Al}_5 \text{V}_3\text{Si}$ can be formed from a low-Si bronze or from a high-Si bronze with a $\text{V}_5\text{Si}_3$ layer. A similar ternary diagram is expected for the
V-Cu-Ge system although it is not clear that there will be a direct tie line
between the A15 phase and the solid solution (Cu-Ge) as in the case of the
V-Cu-Si system.

Finally, there is the case of a section of a ternary phase diagram
where the most stable phase is a phase which bears no relation to the binary
systems. An example is the Nb-Cu-Al system in which two ternary compounds, $x$
phase and a Laves phase $\text{Nb}_x(\text{Al},\text{Cu})_{1-\text{x}}$ block the tie line between the Cu-Al
brass to the Al$_5$ phase. Thus, the superconducting Nb$_3$Al will not be formed at the interface of Nb and a Cu-Al solid solution matrix. The Nb-Cu-Ga system may also be in this category. The ternary section has not been made for this system yet.

In summary, technologically useful single-phase Al$_5$ compounds can only be produced by the "brass process" in the Nb-Cu-Sn and V-Cu-Ga systems. Although possibilities for formation of single-phase layers for other high-$T_c$ compounds exist using quarternary matrices or a new set of matrices without using the Cu-base matrices, it appears that such possibilities are very remote.

B. Kinetics

In this section, the kinetics for the growth of Al$_5$ compound layers at the interface of Nb(V) and the matrix, Cu-Sn(Ga), are treated in detail. First the basic diffusion equations pertinent to the growth are described, and the treatment of the layer growth via a grain-boundary diffusion mechanism by H. H. Farrell et al. is summarized. Then various experimental results related to the growth of the compound layers are discussed.

1. Growth Mechanisms - The purpose of this section is to point out the main considerations for the examination of kinetics of layer growth including the derivation of simple equations for the layer growth rate. For simplicity only the system Nb-Cu-Sn is discussed here, but the formation of V$_3$Ga is essentially the same.

The first step in this discussion is to construct a schematic pseudobinary phase diagram from the ternary Nb-Cu-Sn section (Fig. 6). Since the diffusion paths from Nb and a Cu-Sn solid solution are directly connected to the Al$_5$-phase field, we can make a schematic pseudobinary phase diagram as shown in Fig. 10 and the diffusion path at $\approx 700^\circ$C is indicated. We can consider the diffusion process from two different viewpoints: a) the concentration, and b) the chemical
potential. These are not totally redundant and it is very useful to examine the growth kinetics from both viewpoints. At first, we use the concentration approach, accordingly we consider a planar diffusion couple as shown in Fig. 11a for the analysis of layer growth. In the simplest case, only one element must diffuse across the layer to react with the other element in order for the growth to proceed, assuming Sn alone diffuses, then the compound Nb₃Sn will form at the left interface with a growth rate \( \frac{dX}{dt} = J_{Sn} V_f \) where \( X \) is the thickness of the compound Nb₃Sn, \( t \) is time, \( V_f \) is the volume of Nb₃Sn formed per atom of Sn and \( J_{Sn} \) is the diffusive flux of Sn arriving at the left interface. It is important to note that the Nb-Nb₃Sn interface is moving, so \( J_{Sn} \) is the flux at this interface which is moving. For a constant layer thickness, the flux is given by Fick's law as:

\[
J_{Sn} = D \frac{dc}{dx} \text{Nb-Nb}_3\text{Sn} = D \frac{\Delta C}{X}
\]

where \( D \) is the diffusion constant of Sn in a Nb₃Sn layer, and \( \Delta C \) is the difference in composition across the layer at temperature \( T \). As pointed out by D. S. Kopecki, the exact equation for \( J_{Sn} \) with moving interfaces is almost intractable. However, the form

\[
J_{Sn} = (a\Delta C)/X
\]

is convenient since this will allow us to derive the classical parabolic growth law where \( a = 1 \) for stationary interfaces. It is also likely that \( a < 1 \) for this case.

From Eq. (1) and Eq. (3) the growth-rate equation can be derived as

\[
X^2 = 2a\Delta C V_f t
\]

or

\[
X = \sqrt{K_c t}
\]
and this indicates that the growth in the couple is parabolic since \((2aD_{CV})\)
would be most likely a constant of \(t\).

An alternate approach is to consider the driving force for the growth due to a difference in the chemical potential \(\mu\) across the layer. Then the flux at the Nb-Nb\(_3\)Sn interface is

\[
J_{Sn} = \frac{\alpha M \Delta \mu}{X}
\]

(5)

where \(M\) is the mobility of Sn through Nb\(_3\)Sn. When using this equation, we visualize a couple as shown in Fig. 11b. The point to remember here is that \(\mu\) is continuous across the interfaces when equilibrium occurs at the interfaces. From Eq. (1) and Eq. (5), we again obtain a parabolic growth rate,

\[
dX^2/dt = 2aM_\Delta \mu V_f = K
\]

(6)

Thus, the growth rate of Nb\(_3\)Sn layers should be parabolic with time. However, it should be pointed out that there are some underlying assumptions in the above treatments; it is assumed that: 1) the flux of Sn arriving at the Nb\(_3\)Sn-(Cu-Sn) interface will not be less than \(J_{Sn}\) at the Nb-Nb\(_3\)Sn interface, 2) there is not any diffusion-path-short such as cracks in the layer, and 3) the influence of the Sn concentration in the matrix is not considered.

Early experimental results revealed that the growth of the layer could be either faster, \(^{55}\) slower \(^{56}\) than, or equal \(^{12,13,57}\) to a parabolic dependence with time; e.g., \(X \sim t^n\) and \(n > 1/2, n < 1/2, \) or \(n = 1/2\). As will be discussed in detail in the next section, the large deviations from parabolic growth rate are primarily due to cracks in the layer for \(n > 1/2\) \(^{55}\) and to the depletion of Sn in the matrix for \(n < 1/2\). \(^{56}\) Thus, when the experimental conditions are chosen to avoid these above problems, the growth rate was found to be in most cases parabolic \((n=1/2)\) or nearly parabolic \((n \approx 1/2)\). Thus, it appears that the mechanism for the growth is by bulk diffusion as described by Eq. (4) or (6). However, experimental evidence \(^{58}\) suggests that
the mechanism of growth is diffusion of Sn through Nb₃Sn grain boundaries as originally proposed by Farrell, Gilmar, and Suenaga rather than a bulk diffusion mechanism as assumed above. Thus, we will summarize their analysis for a compound layer growth by a grain-boundary diffusion mechanism in a diffusion couple.

Diffusion along grain boundaries in the absence of compound formation has been theoretically investigated by a number of individuals. In Whipple's formulation, the diffusion in a system containing a single high-diffusivity slab of a width 2a in a semi-infinite medium is described by the equation

$$D \frac{\partial^2 C}{\partial t^2} = \frac{\partial C}{\partial t}$$

in the bulk of the medium, and

$$D' \frac{\partial^2 C}{\partial x^2} + \frac{D}{a} \frac{\partial C}{\partial t} \text{ at } x=0$$

at the slab, where D' is the diffusivity of the thin slab representing the grain boundary. Figure 12 illustrates the geometry of a finite layer, as contrasted to the semi-infinite medium. Calculations using this model indicates that the equi-concentration contours advance with a time dependence appreciably less than the $X_0 \propto t^{1/2}$ law under certain conditions. This is primarily due to the leakage of flux into the bulk. However, when compound formation takes place at the interface, almost the entire flux will be carried to the growth interface and very little is lost to the grains. In fact, under most circumstances, the concentration in the grain boundary approaches steady-state conditions because the motion of the growth front is considerably slower than that of diffusion of atoms at the grain boundaries. Thus, it is expected that a growth interface fed by grain-boundary diffusion will lead to a parabolic time dependence of the layer thickness, as is the case for pure bulk diffusion.
The possibility of nonparabolic growth due to the boundary conditions at the interface in a simplified model was investigated by Farrell et al. Although it is possible to find conditions, in which the time dependence is less than a parabolic one, it requires an unrealistic concentration gradient between the two interfaces; e.g., the concentration of Sn at the Nb-Nb$_3$Sn interface, which is much less than 18 at.%, or a significant leakage of Sn to the grains from the grain boundaries are required for n < 1/2. Thus, it was concluded that, when compound formation is governed by simple grain-boundary diffusion through a "fixed" array of grain boundaries, the growth of the layer will follow a parabolic time dependent formation of compounds with relatively small compositional limits, such as for Nb$_3$Sn.

However, when the rate of the growth is sufficiently slow so that appreciable growth in grain sizes occurs, the total high-diffusivity path area will diminish with time and the flux at the growth front will also decrease with time. In such cases, as shown by Farrell et al. theoretically and experimentally, it is possible to have a nonparabolic growth with time (n < 1/2). This can quantitatively be treated in the following manner. The grain-boundary flux through a series of parallel boundaries of average separation $\bar{L}$ results in the layer growth $X_\phi$ at a rate obtained from the conservation equation

$$\gamma L C_1 \frac{dx_\phi}{dt} = aL' \frac{C_0}{X_\phi},$$

where $aL/\gamma L^2$ is the fraction of the area of the interface occupied by the grain boundaries, and $\gamma$ is a geometrical factor depending on the shape of the grains. $C_1$ is the concentration of Sn at the growth front and $C_0$ is the concentration of Sn above $C_1$ at the original interface. Also, it was assumed that $D \ll D'$. Equation (9) may be integrated to yield
\[ X_t^2 = \frac{2C_o aD'}{C_1 \gamma_0} \int_0^t \left( \frac{L}{L^2} \right) dt \quad (10) \]

or

\[ X_t^2 = \left( \frac{2C_o aD'}{(1-m)C_1 \gamma_0 \lambda_o(T)} \right)^{0.5} t^{0.5(1-m)} \quad (11) \]

where it was assumed that \( L^2 / L = \lambda_o(T)t^m \) and \( \lambda_o(T) \) is a temperature-dependent coefficient. \( m \) is determined by relative values of the activation energies for the grain growth and the grain-boundary diffusion. For the value of \( m \neq 0 \), the growth, \( X_t^2 \), becomes less than a parabolic one. Farrell et al.\(^{53}\) have also shown that in the particular case which they have studied, the contribution from the grain growth toward the reduction of \( n \) less than 1/2 was a significant factor although the nonparabolic-time dependence could not be totally attributed to it.

There is another possibility which leads to a nonparabolic-time dependence of growth kinetics.\(^{54}\) In this case, \( n > 1/2 \). If the flux to the growth interface is greater than required by the kinetics of interfacial processes occurring during the growth of the front, \( n \) can be larger than 1/2 at the very early stage of the growth. Then \( n \) should be 1/2 as the layer increases in size. However, there is no experimental evidence for such an effect; e.g., the reaction for Nb\(_3\)Sn formation is equal or greater than the diffusion rate of Sn through grain boundaries.

Recent study by Togano et al.\(^ {58}\) convincingly showed that the growth of Nb\(_3\)Sn layers is by a grain-boundary diffusion mechanism supporting the theoretical formulation by Farrell et al. as described above. (Also discussed in Section III-B2.) However, there is one very important aspect of the growth kinetics which was not addressed sufficiently by the work of Farrell et al.
This is the influence of the Sn concentration in the matrix on the growth of the compounds. As observed and discussed in Section III-B-2 in both Nb$_3$Sn$^{55}$ and V$_3$Ga$^{61}$ layer growth, the compositions of the matrix have a significant influence on the rate of the compound formation. In the following, a qualitative argument is presented for incorporation of this effect into the grain-boundary diffusion mechanism.

In order to discuss this effect, we have to go back to Fig. 11a and b. There are several possibilities as to what changes for Sn concentration in the layer need to be made when the level of the Sn concentration changes in the matrix. Suppose we initially start with a high Sn concentration, and as the layer grows it will decrease. This can be easily accommodated in Fig. 11a by just changing the level of Sn in the matrix. However, in the corresponding figure (Fig. 11b), the reduction of the chemical potential, $\mu$, in the matrix requires lowering it in the compound at the interface since $\mu$ has to be continuous at the interface. Such reduction may imply that the Sn concentration in Nb$_3$Sn at the interface has to be reduced significantly below 25 at.%. Experimentally, this does not appear to occur since $>$25 at.% Sn in the compound is the most stable composition based on $T_c$ measurements. The next possibility is for Sn in the matrix to retain a large gradient at the interface such that the $\mu$ will remain continuous and unchanged at the interface, but will change at a distance away from the interface in the matrix. Since $D$ for Sn in the bronze is significantly ($\approx 10^2$) larger than that in the Nb$_3$Sn layer, such a gradient is not expected to exist. Furthermore, experimental results$^{62}$ also indicate the absence of such a Sn gradient. Thus, it leaves a possibility that the Sn concentration in the grain boundary is different from the bulk value and it can vary according to the variation of Sn concentration in the matrix.$^{63}$ Such a possibility is schematically illustrated by the dotted lines
in Fig. 11a and b. In this way, the variation of Sn concentration in the matrix can influence the driving force for Sn in the Nb$_3$Sn and thus the growth rate for the layer without changing the bulk concentration of Sn at the Nb$_3$Sn-bronze interface. The result of such a model is that a very even bulk concentration of Sn (~25 at.%) across the layer is expected except very close to the growth fronts where Sn = 13 at.% and ~26 at.%. This is in agreement with early compositional profile measurements and a more recent study (Fig. 13) indicating essentially no change in the composition along the Nb$_3$Sn layers as measured by an electron microprobe and Auger electron compositional analysis, respectively. This modification, however, will not change the results from the grain-boundary diffusion model for the layer growth by Farrell et al. except for the maximum value of $C_0$.

2. Experimental Results

a. Factors influencing growth characteristics - In order to compare existing data on layer growth of the A15 compounds in the bronze process, with the above model, several factors, which critically influence the nature of the growth characteristics, have to be discussed so that those data, which are suitable for the comparison with the growth-kinetics models, can be selected. These factors are the shape of the Nb core, the concentration of Sn or Ga in the bronze matrix, dominant diffusion species, and the grain morphology of the compounds.

In the case of Nb$_3$Sn, it turns out that the shape of Nb core was one of the very important elements in determining the time dependence of the growth. In many experiments, where the depletion of Sn in the matrix during the layer growth is not significant, the growth was substantially faster than $t^{1/2}$ for "circular" Nb filaments of ~10 μm or larger in diameter. However, when "flattened" wires were used for the study, the layer growth was characterized by the $t^{1/2}$ law very well. The difference in this growth
behavior in the bronze-processed Nb₃Sn layer was attributed to the radial cracks formed during its growth. The source of the cracks in the layers appears to be due to the difference in the diffusion rate of Sn and Nb in Nb₃Sn layers. Since Sn migrates to the Nb-Nb₃Sn interface much faster than Nb moving out to the Nb₃Sn-bronze interface, there will be large internal pressures due to formation of Nb₃Sn built up near the Nb-Nb₃Sn interface pushing out the existing Nb₃Sn layer, thus cracking the layer. When cracks are introduced in the layer, they will act as diffusion pipes for Sn and the limiting process will be the formation rate of Nb₃Sn at the Nb-Nb₃Sn interface leading the layer growth νt. A possible evidence for Sn being the primary diffusion species is also provided in the observation of Kirkendall voids at the Nb-bronze interfaces. When Sn moves toward Nb faster than Nb can exit toward the matrix, there will be excess vacancies at the Nb₃Sn-bronze interface which can form voids. Their existence only implies that vacancies are being injected into the bronze (by Sn atoms being injected into the Nb₃Sn) faster than the vacancies can diffuse away to sinks in the bronze, thus giving the required supersaturation. However, if Nb atoms arrive at the bronze-Nb₃Sn interface at the same rate as the Sn atoms move into the Nb₃Sn, the excess vacancies need not be built up at the interface in the bronze. Thus, their existence may be considered as an evidence for the Sn atoms as faster moving atoms than the Nb atoms in the Al5. A composition profile of a Nb₃(SnGa) layer which was measured by a microprobe provided other possible evidence that Sn is the primary diffusion specie. The concentration of Ga in the layer was ~1.5 at.% except near the Nb₃Sn-Nb interface as shown in Fig. 14. At the interface, the Ga level had gone up to ~3.5 at.%. It is assumed that Ga atoms being smaller than Sn atoms can concentrate at the Nb-Nb₃Sn interface to relieve the pressure which is developed by preferential Sn diffusion in the layer.
When flattened wires or tapes were used, the pressure perpendicular to
the tape can be relieved easier owing to essentially a two-dimensional char-
acter of the layer growth in these cases. Thus, no cracks are necessary for
growth of the compound and a parabolic-time dependence of the growth is ex-
pected and found. Furthermore, when the growth rate is significantly slowed
by, for example, using a low-Sn-concentration (<3 at.%) matrix, the time
dependence of growth of the layer becomes nearly parabolic even in the case
of a circular wire. The slow growth rate due to a small driving force for
Sn presumably allows diffusion of Nb to relieve the internal pressure, hence
there will be no crack, and the layer growth is controlled by diffusion rather
than the compound formation rate giving the time dependence of $t^{-0.5}$. It was
observed that the number of Kirkendal voids is less in the composite with a
lower Sn concentration matrix than with a high Sn matrix, thus a slower
growth. This supports the above assumption that the difference in diffusion
rates of Sn and Nb across the layer is less when the growth rate is slower.

In the case of V$_3$Ga, the geometry of the core is not as critical as in
the case of Nb$_3$Sn. From the absence of the Kirkendal voids in multifilamentary
V$_3$Ga wires, it is assumed that the diffusion rates for V and Ga are nearly
equal. This in turn minimizes the development of internal pressures at the
V-V$_3$Ga interface, and thus no cracks will be formed. In most cases, the time
dependence of layer growth was observed to be parabolic. However, when the V cores are alloyed with Zr or Ti (greater than 1-2 at.%), extensive
Kirkendal voids appear at the V$_3$Ga-(Cu-Ga) interface suggesting an increased
Ga-diffusion rate relative to that for V. At the same time, cracks in the
layer are formed and the time dependence of the layer growth becomes significantly
faster than $t^{-1/2}$ as in the case of Nb$_3$Sn.

As stated earlier, another factor which influences the kinetics of the
compound growth is the concentration of Sn or Ga in the matrix. In the
case of Nb$_3$Sn, the dependence of the growth rate of the Nb$_3$Sn layer on the Sn concentration in the matrix is nearly parabolic as shown in Fig. 15a. Since the wires which were used for this study were circular and significant cracks were observed in the layers for Nb$_3$Sn with high Sn contents in the matrix, the true concentration dependence may not be as drastic as indicated in the figure. However, as included in the figure, the data from Wada et al. on "flattened wires" also indicated a nearly identical composition dependence.

Tanaka and Tachikawa reported a very drastic drop with decreasing composition in the growth rate for V$_3$Ga where the cracks did not form. This is shown in Fig. 15b. It is very interesting to note that according to these data, V$_3$Ga will not form in a reasonable range of time and temperature if the concentration in the matrix is reduced below \(13\) at.\%, while Nb$_3$Sn can be formed with the matrix containing \(3\) at.\% or lower Sn. This fact was recently confirmed by reacting a V-(Cu-8 at.\% Ga) composite for 240 h at 700°C and as shown in the figure only a \(0.3\) μm thick layer of V$_3$Ga was formed. This difference is probably a reflection of differences in detailed shapes of the A15 phase fields for Nb$_3$Sn and V$_3$Ga in the respective ternary phase diagrams as discussed in the previous section and in the activities of Ga and Sn in the Cu-alloys. It is somewhat puzzling that essentially all of the data on the growth of pure V$_3$Ga indicate a parabolic dependence on annealing time in spite of such a strong dependence of the layer growth on the Ga composition in the matrix. One would expect to see the effect of Ga depletion on the growth from such data.

Another factor which can influence the growth is the morphology of the grains in the A15 layer. When the compound growth occurs at relatively high temperatures (\(800°C\) for Nb$_3$Sn and \(700°C\) for V$_3$Ga) or with matrices of relatively low Sn or Ga concentration (thus slow growth rates), the layer tends
to consist of columnar grains growing perpendicular to the substrate. Examples of such grain structures in the Nb$_3$Sn layer are shown in Figs. 16 and 17 by transmission electron microscopy and scanning electron microscopy, respectively. As it is discussed later that these layers are highly textured, grain growth is expected to be easy during the layer growth since most of the grains are aligned along similar orientations. Thus, the grain-boundary diffusion path will be decreased with time as the grains grow. Then, the growth rate is expected to slow down ($n < 1/2$) as discussed earlier (Eq. 9).

All of the above indicates to us that in order to obtain meaningful data on kinetics of Nb$_3$Sn layer growth, a large enough matrix to provide nondepleting Sn during layer growth is required, and the shape of the composites should be tapes rather than wires to avoid cracking of the layers. Unfortunately, currently available data on growth usually do not meet these requirements. However, the limited available data tend to indicate that the growth of A15 compound layers by the bronze process depends on heat treating time as $t^{1/2}$ or very close to it. Also, at the time of writing this article, a study is being carried out by the author to investigate Nb$_3$Sn growth kinetics in flat and thick Nb and (Nb-1 at.% Zr)-(Cu-Sn) composites, and preliminary results from this study also point out to $\sqrt{t}$ dependence for both cores when the growth is fast enough to avoid significant grain growth.

b. **Effects of additives on growth characteristics** - In the last several years, extensive studies have been carried out to investigate the effects of minor elemental additions to Nb$_3$Sn and V$_3$Ga in attempts to improve the superconducting properties of these compounds. In this section, only the effects of these additions on the growth characteristics are discussed and the superconducting properties are examined in Section IV. Third or fourth elemental additions can be grouped in two broad categories; additions into a) the core and b) the matrix. A brief review of this subject was also given earlier by Livingston. Among the elements, which are introduced in the Nb
core, there are two types of elements which perform two distinct functions in regard to formation of Nb₃Sn layers. The first type is primarily to pin grain boundaries for enhanced growth of the compound while the second type is to be incorporated in Nb₃Sn primarily to vary the intrinsic superconducting properties, $T_c$ and $H_{c2}$, of the compound.

Zr⁵⁶ and Hf⁸⁰ are the first type. Because (Nb-1 at.% Zr) substrates were used in the liquid diffusion process for fabrication commercial Nb₃Sn tapes, Zr was first tried to study its influence on the critical-current density of the bronze-processed Nb₃Sn wires. In this study, a 0.5 wt% addition to Nb cores enhanced the growth of Nb₃Sn layers by approximately a factor of two from the unalloyed Nb. But a 2.5 wt% addition dropped the growth by ~50% from Nb₃Sn formed using the Nb-0.5 wt% Zr core. However, the time dependence of the layer growth were all approximately $t^{0.35}$. Inferring from the measurements of the critical-current density for these wires, it was concluded that Zr in Nb pinned grain boundaries, and the growth of the Nb₃Sn grains was slowed compared with the Nb₃Sn layer from the unalloyed Nb.⁵⁶ Since the matrix, which was used in this study, was 10 wt% Sn and the core to the matrix ratio was ~3, the growth was rather slow due to probably some grain growth in Nb₃Sn layers and some depletion of Sn in the matrix, thus resulting in $t^{0.35}$ time dependence for the layer growth.⁵³

Recently, Sekine and Tachikawa⁸⁰ reported that the addition of Hf in Nb cores in a matrix of (Cu-7 at.% Sn) increased the growth of the layers by a factor of 2 to 3 from the flattened single-core wires to that of a pure Nb core and the same matrix. (See Fig. 18.) In both cases the layer growth had a parabolic-time dependence. It appears that again Hf helps to slow the growth of the Nb₃Sn grains to increase the growth of the compound as with the Zr addition.
The addition of Ta to the core increased the growth. However, the reason for this increase is not clear. The grain sizes appeared to be approximately equal for pure Nb$_3$Sn and (NbTa)$_3$Sn or to be somewhat larger for the Ta-containing Nb$_3$Sn. The time dependence of the growth was faster than $t^{1/2}$ due to cracks in the layers. Interestingly, the addition of Ta also increased the content of Cu in Nb$_3$Sn layer from ~0.5 at.% at 0 at.% Ta to ~3.5 at.% Cu at 10 at.% Ta in the core. Similar observations have not been reported with the other additional elements in the core.

A number of nontransition elements Ag, Al, Au, Ga, Ge, In, Mg, Sn, and Zn have been added to the bronze (Cu-Sn) matrix to investigate the effects of these additions on the superconducting properties of Nb$_3$Sn. Among these only Ga was incorporated in Nb$_3$Sn layers as mentioned earlier. Small additions of Al and Zn to the matrix enhance growth kinetics, but further additions tend to slow down the growth. The initial increases with the addition of these elements are due to the increased chemical activity for Sn and the decrease is due to decreased availability of Sn in the matrix to keep the bronze in the single-phase region as Al or Zn is added to it. As pointed out, it is reported that Sn's chemical activity is substantially increased by the addition of Zn in a Cu-Sn alloy. When Ag, Au, Ge, and In are added to the matrix, the layer growth is significantly reduced. Furthermore, the matrix addition of Ge results in formation of double layers of Nb$_3$Sn and Nb$_3$Ge$_2$ while the presence of Sn in the core helps formation and also keeps small grain sizes as inferred from $J_c$ measurements of these wires.

A dramatic effect on the growth is observed with a 0.5 at.% Mg addition to the matrix as shown in Fig. 19. The increased growth with the Mg addition is most significant at high temperatures, but the growth is essentially unaltered at ~700°C which is the temperature of most heat treatments for Nb$_3$Sn.
multifilamentary wires. In this study Togano et al.\textsuperscript{58} have clearly identified that the refined grain size in the Nb\textsubscript{3}Sn layer resulting from the Mg added to the matrix is the reason for the enhanced growth, and that the growth is by grain-boundary diffusion in these wires. As shown in the scanning electron micrographs of the Nb\textsubscript{3}Sn layers in Fig. 17, the reduction in the grain size is almost a factor of 3 with Mg addition for the layers which were heat treated at 800°C. However, the difference in the grain size became difficult to distinguish as heat-treatment temperatures were lowered to 700°C, where the growth in both wires became identical. How a small amount of Mg in the matrix refines the grains in Nb\textsubscript{3}Sn layers is not understood at the present time. Using Eq. (10) and assuming no grain growth during heat treatment for the specimen with Mg, they have shown that the thickness of the layer was inversely proportional to the square root of the grain size (the diameter of columns). Also, they found that the time dependences of the layer growth were \( t^n \) where \( n=0.5 \) for Nb\textsubscript{3}Sn with Cu-6 at.% Sn and Cu-6 at.% Sn-0.5 at.% Mg, although \( n \) was somewhat larger than 0.5 for Cu-7 at.% Sn and Cu-7 at.% Sn-0.5 Mg. Thus, they have qualitatively shown that the model developed by Farrell et al.\textsuperscript{53,54} is an appropriate one for describing the growth of Nb\textsubscript{3}Sn in the bronze process although the value of \( n \) larger than 0.5 is somewhat puzzling unless there were some cracks in the layers.

Turning to the bronze-processed \( \text{V}_2\text{Ga} \), only 3 elemental additions, Al\textsuperscript{89,90} and Mg\textsuperscript{91} to the bronze and Ga\textsuperscript{75,90,92,93} to the core, were studied in detail. The results of these additions are summarized in Fig. 20 and Fig. 21b. The addition of Al up to 5 at.% to the bronze (the balance is 15 at.% Ga, 80 at.% Cu) increases the growth of \( \text{V}_2\text{Ga} \) slightly. However, further additions of Al in expense of the Ga resulted in a drastic drop in the layer thickness. Since in this experiment, the total amount of Ga and Al in the bronze was kept constant, it appears that the relative activity of Ga decreased as Ga was substituted by
Al but the growth rate increased due to refinement of the grain size (as inferred by \( J_c \) measurements) by the Al addition. It also appears that the grain size of \( V_3Ga \) is nearly constant beyond a 2 at.% Al addition and the reduced activity of Ga at (12 at.% Ga + 8 at.% Al) in the matrix showed a similar reduced growth as was observed in \( V_3Ga \) which was formed with Ga concentrations less than 15 at.% in the bronze (Fig. 20b). On the contrary, the addition of Al in the V core, slowed the growth kinetics considerably in comparison with its addition to the bronze. The difference appears to be whether Al is incorporated in a \( V_3Ga \) layer or not. In the first case, a very little Al was found in \( V_3Ga \), but in the latter case, a significant level of Al (\( \sim 3 \) at.%) was detected in the layer. Thus, having Al in the core forces Al incorporation in the Al5 structure at the expense of a slowed growth rate which also allowed the increased grain size.

Additions of a small amount of Mg in the matrix and additions of Ga in the V core also increased the layer growth rate significantly. The relative layer thickness with various additions (Al, Ga, and Mg) are compared in Fig. 21. As shown in the figure, the largest increases in the layer growth of \( V_3Ga \) are attained by a 2 at.% Al addition in the 18 at.% Ga bronze and a 0.5 at.% Mg addition in the 18 at.% Ga bronze with a (V-6 at.% Ga) core. Although the increase in the layer growth rate which was obtained by alloying of V with Ga is substantial, it was considerably slower, even at a level of a 9.1 at.% Ga alloying in V, than that which was accomplished with a 0.5 at.% Mg addition to the matrix. It was noted that both additions produce fine and equiaxed grains of \( V_3Ga \). The addition of Ga reduces the total amount of Ga needed to diffuse across the layer below that required in a pure V core, although the same amount of V has to travel to the \( V_3Ga-(Cu-Ga) \) interface. If the growth-limiting process is Ga diffusion, the Ga addition can increase the growth by the reduced total
Ga transport in addition to the reduced grain growth and increased number of easy diffusion paths. In the case of Mg addition, the increased growth rate is solely due to the refinement of the grain size. Apparently, Mg was only detected in the half of the layer which is adjacent to the Cu-Ga-Mg. But it is not clear how Mg only in one half of the layer can influence the growth of the other half. The activation energies, $\Delta G$, for the layer growth, which were determined by $X_0^2/t = A \exp(-\Delta G/kT)$ are identical for a pure V and Ga-containing cores ($5.4 \times 10^{-19}$ J) but was reduced ($4.9 \times 10^{-19}$ J) when Mg was added. Perhaps, Mg may also increase diffusivity of Ga and V in grain boundaries in addition to increasing the number of grain boundaries. Such a notion is consistent with the observed $J_c$ for these wires; i.e., $J_c$ for (a) V$_3$Ga with the (V-6 at.% Ga) core and the matrix without Mg is higher than that for (b) V$_3$Ga with 0.5 Mg in the matrix and a pure V core, however, the growth rate for (b) is faster than (a). Assuming $J_c$ to be inversely proportional to the grain size, the results of the growth rate and $J_c$ (9.5 Tesla) for these wires are inconsistent unless an enhancement of boundary diffusion by Mg is considered to cause the increased growth rate in the Mg-containing V$_3$Ga composites.

Although it was reported that the additions of Ga and Mg increased the Ga content in V$_3$Ga from 22.5 to 23.5 at.% for V$_3$Ga without and with the additions, respectively, there was not enough $T_c$ change ($\approx 0.3$ K) to be consistent with such a large increase in the Ga content. According to Das et al., a change of $\approx 1$ K is expected for the reported concentration change.

The time dependence of the growth was, in all cases which were discussed above, parabolic. The only instance that the parabolic-growth rate is violated is when Zr in sufficient amounts was added to the V core. The addition of Ti probably also makes the dependence nonparabolic but sufficient data are not available at this time.
There are other Al5 compounds which can be formed by the bronze process such as V₃Si₆⁹⁶,⁹⁷ V₃Ge₉⁸ and V₃(GeAl).⁹⁹ All of these compounds can only be formed in two-phase layers except in the case of V₃Si when the content of Si is sufficiently low. The phases V₅Si₃ and V₅Ge₃ are the major phases at the interface. Moreover, V₃(GeAl) is only formed at the interface of the (V-Al)-(V₃Ge) and it is so thin that it cannot be observed with a scanning electron microscope. All of these composites are not of practical interest and will not be discussed any further.

c. Morphology of compound grains - As already mentioned above, the morphology of the grains which are formed in the bronze-processed Nb₃Sn and V₃Ga is important in understanding the critical-current density and growth kinetics of these compounds. For these reasons, a number of studies were carried out to examine grain morphology and sizes and growth textures for Nb₃Sn and V₃Ga. These results are summarized here. The influence of the grain size on the critical-current density is discussed later.

Grain sizes and shapes reported for the bronze-processed Nb₃Sn and V₃Ga differ somewhat from investigator to investigator and depend on the techniques employed for observation. However, they strongly depend on the processing conditions, such as heat-treating conditions, concentrations of Sn or Ga in the matrix, the extent of deformation in the filaments of Nb or V, etc. For a comparison of grain-growth kinetics and of the critical-current densities in Nb₃Sn, V₃Ga, and V₃Si, Livingston⁹⁷ carried out an experiment to study the grain size and its relationship to the critical-current density in these superconductors using identical flattened 19-core (20 μm) filamentary composites. He found that the grains in all of the compound layers were equiaxed, and that V₃Ga grains grew considerably faster than Nb₃Sn and V₃Si for reaction temperatures above 650°C as shown in Fig. 22. He speculated that the difference is due to a lower homologous temperature for V₃Ga (which is stable only up to
about 1300°C) than for Nb₃Sn and V₃Si (which are stable to over 2100°C). Thus, thermodynamic driving forces for nucleation of new grains are higher for Nb₃Sn and V₃Si and the diffusivity of Ga and V higher for V₃Ga. Both may contribute to the larger grains found in V₃Ga.

In contrast to the above observation, Farrell et al. found a columnar growth in a 19-core Nb₃Sn which was formed at 800°C. Runde also found columnar grains in a fine multifilamentary wire heat treated at 750°C for 24 h as shown in Fig. 16 although the region at the interface with the matrix contains grains which are less columnar in shape. Scanning-electron-microscopic observations of similar Nb₃Sn multifilamentary wires as well as monofilamentary Nb₃Sn and V₃Ga wires indicate that the compound layers which were formed at high temperatures showed a greater tendency to be columnar than those formed at lower temperatures. However, in contrast to the above observations, West et al. found for multifilamentary Nb₃Sn wires by an electron-transmission-microscopy technique that those grains which were grown at lower temperatures tend to be more columnar than those which were grown at higher temperatures.

It is difficult to determine the causes for these contradictory observations regarding the differences in the morphology of Nb₃Sn grain structures. In general, the tendency for equiaxed-grain growth is greater if the growth rate of the layer is increased by higher contents of Sn or Ga or certain additives such as Mg, Zr, etc. in the matrix or the core, and sufficient amounts of the matrix to avoid depletion of Sn and Ga during the layer growth.

The textures in the bronze-processed as well as in the surface-diffusion-processed Nb₃Sn and V₃Ga tapes were measured and reported by Togano et al. The Nb₃Sn layers and the substrates, V and Nb, of the bronze-processed V₃Ga and Nb₃Sn exhibited very strong (100) <011> texture. In the surface-diffusion processed V₃Ga, they noted that the texture did not change while the grain morphology varied from equiaxed to columnar growth with decreasing heat-
treatment temperatures. Also the texture was found not to change with the depth into the layer in these $V_3Ga$ tapes. Unfortunately, a similar experiment on the influence of reaction temperature on texture has not yet been conducted on the bronze-processed $Nb_3Sn$ and $V_3Ga$ wires nor tapes. It would be of interest to investigate texture in these compounds formed on fine wires and with alloyed matrices and cores to see whether similar textures exist in the wires as in the tapes.

IV. Influence of Metallurgical Factors on Superconducting Properties

In this section, various metallurgical factors influencing the superconducting properties of the bronze-processed Al15 superconductors are discussed. First, the effect of compressive strains on the critical properties of these compounds are pointed out so that $T_c$, $J_c$, and $H_{c2}$ of these wires can be compared more meaningfully.

A. Strains in Composite Superconductors and Their Influence on the Superconducting Properties

The fact that filamentary Al15 superconductors are made by a solid-diffusion process and thus are in a composite form has a great significance in the way which their superconducting properties are determined. One manifestation of this is the existence of compressive strains in the compounds due to a larger thermal-expansion coefficient for the matrix than for the cores. This effect is best illustrated in Fig. 23 which plots $T_c$ changes, as the matrix is removed by chemical etching, for four Al15 compounds fabricated by the bronze process as a function of the matrix-to-core ratio. Here the difference in $T_c$ is defined as $[\Delta T_c = T_c$ (with the matrix) $- T_c$ (without the matrix)]. As shown in the figure, the presence of the matrix can increase or decrease $T_c$ as much as $\sim 2$ K except in the case of $V_3Ga$, which does not vary
significantly, and this points out one very important aspect of variation in superconducting properties in the as-prepared superconducting composites depending on the ratio of the matrix to the core.

First, a brief description of strains in the compound layers in these composite wires is given to facilitate the following discussion on variations in the critical properties. (A detailed analysis of strains in these wires and tapes and related changes in superconducting properties is given by D. O. Welch.\textsuperscript{26}) As mentioned earlier, when a composite wire consisting of Nb, Nb\textsubscript{3}Sn, and a Cu-Sn alloy matrix (Nb\textsubscript{3}Sn is used for an example for convenience for this section) is heated at elevated temperatures (\textasciitilde700°C) and cooled to low temperatures (\textasciitilde4 K), there will be stresses and strains in each component of the composite. These stresses and strains result from differential thermal expansion of the components. Since the expansion coefficients \( a \) for Nb and Nb\textsubscript{3}Sn are essentially identical, we only consider the difference between those for the core (Nb and Nb\textsubscript{3}Sn) and the matrix. Then, based on force and length balance, the longitudinal strain \( \varepsilon_c \) in the core is given by

\[
\varepsilon_c = -\Delta \alpha \Delta T \left( \frac{E_m}{E_c} \right) \left( R^{-1} + \frac{E_m}{E_c} \right)^{-1}
\]

where \( E_m \) and \( E_c \) are Young's modulus for the matrix and the core, respectively, and \( \Delta \alpha \), and \( R \) are the differential-thermal-expansion coefficient between the core and the matrix, and the volume ratio of the matrix (bronze) to the core, respectively. For simplicity only the strain which is induced along the length of wire is considered. (It was shown that the radial strain in the wire is nearly zero.\textsuperscript{28}) Also, neglected here are the effects of plastic strain of the matrix as well as the Nb core at moderate temperatures during the cooldown process.\textsuperscript{28,103}

Following the phenomenological development by Testardi\textsuperscript{104} and Welch,\textsuperscript{28} we simply assume that the critical-temperature dependence on strain is
\[ \Delta T_c = -A\varepsilon_c^2 \quad (13) \]

where \( A \) is a proportionality constant. If \( E_m = E_c \) is assumed. (This assumption may not be correct at low temperatures as shown by Bussiere et al.\textsuperscript{105} that the modulus for \( \text{Nb}_3\text{Sn} \) is decreased by a factor of 2 as temperature is lowered to \( \nu T_c \) and below.)

\[ \Delta T_c = -A(\Delta\alpha\Delta T)^2 \left[ \frac{R}{1+R} \right]^2 . \quad (14) \]

Thus, the reduction in \( T_c \) due to the matrix compression is parabolic with \( (\Delta\alpha\Delta T) \) and \( R \) for small values of \( R \). For large values of \( R \), \( \Delta T_c \) only depends on \( (\Delta\alpha\Delta T)^2 \). The observed \( \Delta T_c \) dependences on \( R \) in Fig. 23 are qualitative agreements with Eq. (14).

The influence of the compressive strain on critical-current densities at high magnetic fields and critical magnetic fields are shown in Figs. 24\textsuperscript{106} and 25.\textsuperscript{106} In these cases, the compressive strain in each wire was varied by varying the \( R \) values. It is not clear whether the dependence of \( J_c(H) \) on strain is due to only changes in \( T_c \) or to other additional factors such as strain induced flux pinning sites in \( \text{Nb}_3\text{Sn} \).\textsuperscript{107} The variation in \( H_{c2} \) with strain is shown as \( H_{c2}/T_c \) vs \( R \). An analysis\textsuperscript{(28)} based on GLAG theory shows that \( H_{c2} \) should be more sensitive to strain than \( T_c \) but how much more depends on details such as the strain sensitivity of the density of states, phonon anharmonicity and other factors which are not well understood at this time.

Synergistic effects of alloying and disordering of the compounds on the strain sensitivity of superconducting properties have also been observed. When \( \text{Nb}_3\text{Sn} \) was alloyed with Ga by an addition of Ga to the Cu-Sn matrix, \( \Delta T_c \) for \( \text{Nb}_3(\text{SnGa}) \) was significantly reduced\textsuperscript{108} while the addition of Ta to the compound increased \( \Delta T_c \) from 1.0 K for pure \( \text{Nb}_3\text{Sn} \) to 2.2 K for \( \text{Nb}_3\text{Sn} \) from a Nb-10 wt% Ta core when the wires were heat treated for 16 h at 725°C.\textsuperscript{109}
Earlier, it was shown that $\Delta T_c$ for a given wire decreased with increasing annealing time at 725°C, indicating that the disorder in $\text{Al}_5$ structure also increased the sensitivity of $\text{Nb}_3\text{Sn}$ to the strain. This observation was further clarified by studying $\Delta T_c$ as a function of neutron irradiation, and the result is shown in Fig. 26. The physical mechanism for these observed strain sensitivities in $\text{Nb}_3\text{Sn}$ by alloying and disordering is not known at this time.

Furthermore, the geometrical configuration of filaments can also influence the reduction of $T_c$ by the compressive strains. As mentioned earlier, when the bronze is placed inside Nb tubings, the $\text{Nb}_3\text{Sn}$ layer formed at the interface will experience a significant radial strain even for a rather small value of $R$. This can also lead to a large reduction in $T_c$ for a wire with a small $R$. All of these above examples indicate that superconductivity in the $\text{Al}_5$ structure is in general very sensitive to nonhydrostatic strains. Therefore, when any of the critical superconducting properties for various specimens are compared, all of these factors, which can influence the properties of as-prepared wires, should be carefully examined.

### B. Critical Temperatures

Superconducting critical temperatures of $\text{Nb}_3\text{Sn}$ and $V_3\text{Ga}$ which are produced by the bronze process depend on a number of parameters, reaction time and temperatures, compositions of the tube, filament sizes, compressive strains, etc. Unfortunately, many of these variables are related to the others and it is difficult to separate out each parameter and examine its influence on $T_c$ for these compounds. In this section, an attempt is made to distinguish various variables and to measure their influence on $T_c$ for $\text{Nb}_3\text{Sn}$ and $V_3\text{Ga}$. Metallurgical effects on $T_c$ for $V_3\text{Si}$, $V_3\text{Ge}$, and $V_3\text{GeAl}$ are not included in this discussion since these compounds are of little value to practical applications. Initially, the discussion will primarily focus on
effects of heat treatment, and then the influence of the alloy additions on $T_c$ are discussed.

1. **Effects of Heat Treatments** - The critical temperature generally increases with increasing heat-treating time at a given temperature. This is illustrated in Figs. 27 and 28 for two filament sizes, a monofilamentary wire (core $\approx 150$ um) and a fine multifilamentary commercial wire (filament $\approx 3$ um), respectively. It is interesting to note that in both cases, $T_c$ of Nb$_3$Sn reaches 17.9 K after 6 h at 725°C when all prestrains due to the matrix are removed. This indicates that Nb$_3$Sn which was formed in such a short period has already established a relatively high degree of the crystallographic order in a substantial portion of the layer. [Very thinner layers ($<1$ um) tend to have lower $T_c$. This, according to Auger chemical analysis and profiling of Nb$_3$Sn layers, is due to a deficiency of Sn in the layer.] The detailed comparison between these two figures indicates that $T_c$ in the multifilament wire increased faster than $T_c$ in the monofilament wire implying the order in Nb$_3$Sn can establish faster when the filaments are fine. This is probably due to completion of reaction for formation of Nb$_3$Sn which is accomplished in a shorter time with fine filaments. When the reaction is completed, only atomic motion required is for the ordering process, while it may take a growth of a certain thickness of Nb$_3$Sn layer before a section of well-ordered Nb$_3$Sn is made during the growth if the entire Nb is not consumed for Nb$_3$Sn. It is also interesting to note that $T_c$ with the matrix-on can give an indication of a relative order in Nb$_3$Sn. In other words, the depression in $T_c$ due to the matrix is larger if the ordering in Nb$_3$Sn is less as observed in Figs. 27 and 29.

Other phenomena related to the strain effect on $T_c$ is that the $T_c$ of a given multifilamentary wire may keep gradually increasing with time. One should be aware of the fact that the Sn concentration in the matrix decreases,
and thus the yield stress of the matrix decreases with time as the layer grows. This in turn decreases the strain in $\text{Nb}_3\text{Sn}$ and results in a higher $T_c$ of the wire. Earlier, the increases observed in $T_c$, $H_{c2}$ and thus high-field $J_c$ with longer heat treatments was thought to be only associated with the increased ordering in $\text{Nb}_3\text{Sn}$. But the $T_c$ without the matrix reaches its maximum value in a very short time and thus, it appears that an additional reason for increased $T_c$ and $H_{c2}$ for longer-time heat treatments is due to the softening of the bronze and therefore a smaller compressive strain in $\text{Nb}_3\text{Sn}$.

$T_c$ of $\text{Nb}_3\text{Sn}$ is a function of the temperatures at which it is formed. Unfortunately, it is difficult to find a unique parameter with which to study the influence of the reaction temperatures on $T_c$ since $T_c$ also depends on the reaction time, and comparing $T_c$ of the wire which is formed at several temperatures for a constant heat-treatment period is not a good choice since for a given period the compound may hardly grow at a particular temperature and yet at high temperatures it may become completely reacted. A reasonable choice for this is $T_c$ at a constant thickness, but it unfortunately turns out that there are no published $T_c$ data on $\text{Nb}_3\text{Sn}$ which are given for a constant thickness of $\text{Nb}_3\text{Sn}$ layers at various temperatures. Perhaps, the best way to study the influence of the heat-treating temperature on $T_c$ is to use fine multifilamentary wires and to react all of the Nb filaments at each temperature. In addition, at each temperature, heat-treatment time is long enough such that $T_c$ of the wire with the matrix removed does not vary in a further heat treatment. The work by Aihara does not meet this criterion completely but this is the best study available in investigating $T_c$ of $\text{Nb}_3\text{Sn}$ as a function of the reaction temperature. This is shown in Fig. 29a. $T_c$ is essentially constant between 650°C to 800°C but drops drastically beyond 800°C. A slight lowering of $T_c$ at 650°C may be due to a smaller thickness
of Nb$_3$Sn which was obtained for this temperature than all the others. But others also observed a slight decrease in $T_c$ for the wires reacted at 650°C from those reacted at higher temperatures. Smathers et al. concluded that based on their Auger-chemical analysis of the layer the drop in $T_c$ at 650°C is due to the compound being not at stoichiometry. Also shown are the corresponding lattice parameters $a_0$ for each Nb$_3$Sn layer (Fig. 29b). As expected $a_0$ decreases with the temperature above 800°C. Aihara concluded that the primary reason for the drop is that Nb occupying the Sn sites, although other possibilities such as inclusion of Cu or vacancies in the Sn sites cannot be eliminated. The disordering in Nb$_3$Sn due to the site exchanges between Nb and Sn is less likely since high-$T_c$ Nb$_3$Sn can be made by physical vapor-deposition techniques as high as 960°C unless the presence of Cu can promote such exchange.

The composition of the matrix is known to affect $T_c$ of V$_3$Ga (see below), but unfortunately, there is not any experiment systematically studying such effects on the $T_c$ of Nb$_3$Sn. However, observing $T_c$ for Nb$_3$Sn wires which are made from a Cu-13 wt% Sn and 1-10 wt% Sn, the effect appears not to be a large one if a constant-compound-thickness criterion is employed for the layer greater than 1-2 μm thick.

In the bronze-processed V$_3$Ga, effects of heat-treating time on $T_c$ were studied for 3 bronze matrices with 15, 18, and 20 at.% Ga and the results are shown in Fig. 30. For V$_3$Ga which was formed with 18 and 20 at.% Ga bronzes, $T_c$ reached ~15 K within 1 h at 700°C. However, if a 15 at.% Ga bronze is used for the matrix, it took over 100 h for $T_c$ of V$_3$Ga to reach ~15 K. This result was replotted on a constant-thickness basis in Fig. 31 and it points out that $T_c$ is not only a function of V$_3$Ga thickness but also of the composition of the matrix from which the compound is made from. Also included in the figure
are the data from Berthel et al., showing their observation of the composition dependence which is similar in shape but somewhat lower in $T_c$.

The influence of the reaction temperatures on $T_c$ of the bronze-processed $V_3Ga$ was studied by Suenaga and Sampson, and Howe et al. Their results are shown in Fig. 32 where $T_c$ for $V_3Ga$ at thicknesses of $\sim 1$ $\mu$m and $\sim 2.5$ $\mu$m was compared for different temperatures of formation. Interestingly, the value of $T_c$, which was measured by Suenaga and Sampson for $V_3Ga$ ($\sim 1$ $\mu$m) from a (15 at.% Ga) bronze and a pure V core, matched exactly the values measured by Howe et al. in $V_3Ga$ from a (18 at.% Ga) bronze and a V-8 at.% Ga core. This indicates that there is a very small effect of the bronze composition difference on $T_c$ of $V_3Ga$ at least at 600°C in contrast to the results by Tanaka et al. These contradictory observations in the dependence of $T_c$ on the bronze composition and the thickness appears to be due to the difference in the reaction temperature. At lower reaction temperatures, the influence of the thickness and the composition for a constant thickness on the $T_c$ becomes less.

Unfortunately, in all of these studies, there were no accompanying investigation of the lattice parameter or careful microprobe chemical analysis related to the observed variations in critical temperatures. Thus, it is very difficult to speculate about the reasons for the $T_c$ variations in $V_3Ga$ with the bronze composition and heat-treating conditions. As shown by Das et al., a $V_3Ga$ can be formed with either excess vacancies or V at the Ga sites, thereby lowering the value of $T_c$ from the stoichiometric value. Thus, the lowered $T_c$ under certain conditions as seen above may be due to one of these possibilities as well as inclusion of Cu in the compounds.

Finally, it is very obvious from the above discussion, there still exists a need for careful and thorough studies on the clarification of the influence of heat-treatment conditions on $T_c$ of both $Nb_3Sn$ and $V_3Ga$ in the bronze-processed wires.
2. **Effects of Additives** - Elemental additions to Nb$_3$Sn can be classified in two groups. They are the transition and the nontransition elements: Zr, 56, 80, Hf, 80, and Ta, 70, 71, 109, and Al, 67, 68, Ga, 80, 83, In, 68, Si, 68, Ge, 84, 85, Mg, 58, Sn, 66, and Zn, 71 respectively. All of the transition elements are introduced in the core as alloys, and they are incorporated in the compound layers. Although the exact location of these alloying elements in the crystallographic sites are not known, it is expected that these are primarily substitutional elements for Nb rather than for Sn. It appears that only one half of the amount of Hf in the core is used in alloying Nb$_3$Sn while essentially all of Ta in the core is incorporated in the layer. 70 Sekine and Tachikawa reported that the additions of both Zr and Hf increased $T_c$ of the compound up to $\sim 0.5$ over $T_c$ for pure Nb$_3$Sn produced by the bronze process, when it was formed at 800°C for 100 h. On the contrary, the additions of 0.5 and 2.5% Zr to the core was found to decrease resistively measured $T_c$ by $\sim 0.2$ K, and with Zr additions significantly thicker layers are required to achieve a saturation of $T_c$. For example, 17.8 K for $T_c$ of the pure Nb$_3$Sn was reached at $\sim 1.5$ μm thick layer while $T_c$ of 17.6 K for Nb$_3$Sn with 0.5 or 2.5% Zr in the core was obtained at a $\sim 7$-μm thick layer when these wires were heat treated at 700°C. The above apparent contradiction could be the result of the difference in the reaction temperatures. In the latter study, it was also found that $T_c$ for Nb$_3$Sn with 0.5% Zr in the core only reached $\sim 17.2$ K at $\sim 7$ μm layer thickness when it was formed at 650°C. Perhaps, these results indicate that the crystallographic order in Nb$_3$Sn is more difficult to achieve for a constant layer thickness in the presence of alloying elements such as Zr when the reaction temperature is lower than when it is higher. The influence of the strains on $T_c$ in Nb$_3$Sn alloyed with Zr or Hf is still unknown. A possible reason for the increase of $T_c$ with the Zr and Hf additions is due to changes in the precompressive strain from the matrix. Since the $T_c$ results are quoted
for a constant reaction time (100 h) in the study by Sekine and Tachikawa, the thicknesses of the compound layers with the additions are significantly greater. Zr (Nb₃Sn ~18 μm, and Nb₃Sn with 2 at.% and 5 at.% Hf in the core ~32 μm and ~60 μm, respectively.) These differences in the thickness reflects the difference in the remaining Sn in the matrix and thus its yield stress. When the layer is thicker, the matrix yields at a lower strain. Then, the precompression in the Nb₃Sn is smaller, and Tc reduction due to the matrix is less. Therefore, the observed increases in Tc with the Zr and Hf additions need to be reexamined with the matrix off to clarify the influence of these additions and the reaction temperature on Tc of Nb₃Sn.

The effect of Ta addition to Nb₃Sn through core alloying was carefully studied, and the result is shown in Fig. 33. It is interesting to note that a small addition (~1.5 at.%) of Ta increased Tc of Nb₃Sn by ~0.3 K, but this increase in Tc was only revealed after the matrix was removed since Tc with the matrix intact monotonically decreased with the Ta concentration in the core. Also, the differences in Tc with heat treatment time at 725°C are very much greater with the matrix than without as mentioned for the pure Nb₃Sn; i.e., the reduction in Tc is greater in the disordered Nb₃Sn than in the ordered Nb₃Sn. This example again clearly points out the importance of the prestrain from the matrix in determining Tc of the wires and in understanding variations in Tc with heat treatment and alloying. Another interesting aspect of this study is that the strain sensitivity of Nb₃Sn as measured by Tc for the wires with and without the matrix increased with small Ta additions but at high alloying contents of Ta in Nb₃Sn it decreases approximately to the value for the unalloyed Nb₃Sn. The mechanism causing such variation is not understood yet at the present time.

In contrast to the transition-element additions, the nontransition elements are not easily incorporated in the compound Nb₃Sn when these elements
are either added to the matrix or to the core. One exception to this generality is Ga. As discussed earlier, Ga is incorporated in the compound at a level of 1 to 1.5 at.% \(^{80,88}\) and the inclusion of Ga raised \(T_c\) of the compound \(\sim 0.3\) K over the value for the pure Nb\(_3\)Sn. Furthermore, this increase was maintained when the matrix was removed, \(^{108}\) thus it is not due to the prestrain. A small addition of Mg to the matrix increased the growth of the compound but no trace of Mg in the compound was found in the Nb\(_3\)Sn layer and no influence on \(T_c\) due to the addition was noted. \(^{58}\) However, all other additions tend to slow down the time to reach the maximum \(T_c\) (\(\sim 17.5\) K) at a given temperature. As in the previous cases, it is very difficult to assess the influence of these additives on \(T_c\) since none of the reports on \(T_c\) was based on constant thickness. Furthermore, \(T_c\) was not measured without the matrix in any studies.

For \(V_3Ga\), the influence of the additions of Ti, \(^{95}\) Hf, \(^{113}\) Mg, \(^{91}\) Mn, \(^{114}\) Al, \(^{89}\) and Si \(^{115}\) were studied, and in all the cases, \(T_c\) of \(V_3Ga\) was not significantly affected by these additions except in the case of Si which drastically reduced its \(T_c\).

C. Critical-Current Densities and Magnetic Fields

With the increasing importance of multifilamentary Nb\(_3\)Sn and \(V_3Ga\) conductors for technological uses such as for the production of very high magnetic fields in fusion magnets, means of improving the superconducting critical-current density \(J_c\) have been sought intensively, and it has been found that metallurgical factors such as heat-treatment conditions, \(^{56}\) alloying additions, \(^{9}\) and mechanical strains \(^{28}\) can strongly influence the critical-current density. The correlation of changes in \(J_c\) with such metallurgical variations in the Nb\(_3\)Sn wires has been facilitated by the use of scaling laws for magnetic flux pinning in hard superconductors.

In this section, the most commonly used scaling law \(^{116}\) for magnetic flux pinning is described, and its applicability to the bronze-processed Nb\(_3\)Sn wires
is critically examined. (Since this particular scaling law does not apply
to the paramagnetically limited superconductors such as \( V_3Ga \), this discussion
is limited to \( Nb_3Sn \) wires.) Because the way in which \( H_{c2} \) is determined is very
critical to the scaling of flux pinning, and because \( H_{c2} \) can influence the high-
field \( J_c \) strongly, the discussion of \( H_{c2} \) is combined with that of \( J_c \). The
dependencies of \( J_c \) for \( Nb_3Sn \) and \( V_3Ga \) wires on temperature and the grain size
are also discussed in this section, followed by the summaries on the influence
of heat treatments and alloy addition on \( J_c \) of \( Nb_3Sn \) and \( V_3Ga \) wires.

1. Flux Pinning (the Scaling Law) - Flux pinning studies\(^{116-119}\) of
type-II superconductors have indicated that the variation of the bulk pinning
force density, \( F_p = |J_c \times \vec{H}| \), with magnetic field and temperature can be de-
scribed by an equation

\[
F_p = AB_{c2}^m(T)f(h) \tag{15}
\]

where \( A \) is a constant independent of \( T \) and \( h (=H/H_{c2}) \), but is a function of
the microstructure in superconductors. \( m \) is a numerical constant and may vary
with microstructural changes. \( f(h) \) can be rewritten as \( f(h) = h^2(1-h)^n \) and
\( l \) and \( n \) may change from one superconductor to another. In the investigation
of \( Nb_3Sn \) wires, the scaling law developed by Kramer\(^{116}\) has been used frequently.\(^{120,121}\)
Thus, we will first briefly summarize the features of the scaling law, and point
out those instances where the equation appears to work well and other cases
where the use of the equation leads to unrealistic results.

According to the Kramer's model\(^{116}\) the magnetic flux pinning strength, \( F_p \),
can be discussed in terms of two regimes: high and low magnetic field regions,
which are given by Kramer as

\[
F_p = |J_c(H) \times \vec{H}| = K_s h^{1/2}(1-h)^2 \tag{16}
\]

and
for the high- and low-field regions, respectively, where

\[ h = \frac{H}{H_c}, \quad K_s = 0.56 \frac{H^2}{c^2} K_1^{-2} (1 - a_0 \sqrt{\rho})^{-2}, \]

\[ K_p = 5 \times 10^6 \rho \beta \sqrt{\frac{4}{\pi}} \frac{4 H}{c^2} \frac{1}{K_1}, \]

and \( a_0 \) is the flux lattice spacing \( a_c = (\frac{\rho}{H})^{1/2} \) and \( \beta \) is the density of flux-pinning sites, \( c \) is a constant, \( \omega \) is the net number of pinning sites per unit length of flux line in the low-field regime, and \( P \) is approximately constant. This equation was derived assuming that flux pinning could be described by two regimes: at low fields flux motion occurs primarily by unpinning, whereas at high fields flux motion occurs by synchronous shear of the flux line lattice around pins too strong to be broken. Furthermore, the equation describes the dynamic pinning force produced by a series of pinning planes, each of which consists of a series of line pins, and which lie parallel to the Lorentz force.

In the past, the scaling law has often been tested by plotting experimental data as \( F_p/F_{p\max} \) vs \( h \) or \( F_p \) vs \( h^{1/2}(1-h)^2 \). A difficulty associated with such plots is the determination of a consistent value of the upper critical field \( H_{c2} \), needed to calculate the reduced magnetic field \( h \) appearing in Eq. (15). Also, when both axes are normalized, it is not easy to make a critical comparison.

For studying the high-field behavior of \( J_c \) or \( F_p \), it is found that another form of Eq. (16) is more convenient and useful. Simple algebraic manipulation of Eq. (16) yields:

\[ J_c^{1/2} H^{1/4} (1 - a_0 \sqrt{\rho}) = 0.7 K_1^{-1} (H_{c2} - H). \]
In most cases, at sufficiently high field, \( a_0 \sqrt{H} \ll 1 \), \( J_c H^{1/2} H^{1/4} \) is linear in
\( H \) over a reasonably wide range of \( H \); thus \( H_{c2} \) is obtained simply by linear
extrapolation and the Ginzburg-Landau parameter \( \kappa_1 \) is obtained from the slope
of the plot without adjustable parameters. In the following section, the
applicability of the scaling law, in the form of Eq. (18), is examined for
bronze-processed \( \text{Nb}_3\text{Sn} \) wires with regard to: 1) the linear dependence of
\( J_c H^{1/2} H^{1/4} \) on \( H \), and 2) the values of \( \kappa_1 \) determined from the slope.

In order to examine the applicability of the scaling law to the bronze-
processed wires, the first, \( J_c \) data for a composite monofilamentary wire with
a matrix-to-core ratio of \( \approx 15 \) and with a heat treatment of \( 725^\circ C \) for \( 120 \) h
are plotted in Fig. 34 as suggested by Eq. (18), illustrating its use in
analyzing the magnetic field dependence of the critical-current density.
Here it was assumed that \( a_0 \sqrt{H} \ll 1 \) in calculating the left-hand side of Eq.
(18), and this assumption seems to be justified since the plot is a straight
line with \( H \) over a wide range in magnetic field (\( \approx 8 \) to \( \approx 16 \) \( T \)). This implies
that the distance between the pinning sites in this wire is considerably larger
than the flux lattice spacing, \( a_0 \). Therefore a measure of the upper critical
field \( H_{c2} \) can be obtained by the linear extrapolation of the straight segment
of the plot. This value of \( H_{c2} \) is not the magnetic field where superconduc-
tivity vanished totally from the wire, as may be seen in the figure. The
experimental data deviate from a straight line near the critical field. In
fact, superconductivity persists to considerably higher values (\( \approx 2 \) \( T \)) than
the \( H_{c2} \) as determined by linear extrapolation. This is probably due to in-
homogeneities in the \( \text{Nb}_3\text{Sn} \) such as a composition variation across the \( \text{Nb}_3\text{Sn} \)
layer or a variation in the strains due to the matrix.\(^{28}\) It is also possible
that the bulk of the \( \text{Nb}_3\text{Sn} \) still carries superconducting currents beyond the
extrapolated \( H_{c2} \), and that the dependence of \( J_c \) on \( H \) does not follow Eq. (18)
in that region; i.e., the scaling law fails here. Although the values of \( H_{c2} \)
obtained by extrapolation will differ from those determined with other criteria,
such as the midpoint of the transition from the normal to the superconducting state, $H_{c2}$ as determined by this method will be consistent with Eq. (13) for the purpose of examination of the validity of the scaling law. Thus, in the following discussion, the values of $H_{c2}$ quoted were all determined by the linear-extrapolation method, unless stated otherwise.

In the majority of cases, our measurements on monofilamentary Nb$_3$Sn wires show that $J_c$ varies with magnetic field as described by Eq. (18) with $a_o \sqrt{\rho} << 1$, and thus yield linear plots of $J_c^{1/2}H^{1/4}$ versus $H$ (except very near $H_{c2}$) as shown in Fig. 34. However in several instances, such simple quasilinear plots were not obtained, and we believe such deviations fall into two categories.

In the first category, a plot of $J_c^{1/2}H^{1/4}$ versus $H$ yields a plot with concave-up curvature. We believe that such curvature results from the erroneous assumption that $a_o \sqrt{\rho} << 1$. This behavior is illustrated in Fig. 35 which show data for an "in-situ processed" wire, heat treated at 550°C for 6 days. A similar result was also obtained for a "bronze processed" Nb$_3$Sn wire which was electron irradiated during a 500°C heat treatment. As shown in the figure, the data can be made to produce a wide region of linearity in the plot if the $(1-a_o \sqrt{\rho})$ term is included. Also in both cases, the selection of $(10^3 \text{ Å})^{-1}$ for the value of $\sqrt{\rho}$ resulted in a linear dependence on $H$. This value was found to give a better straight-line fit than is obtained with $(500 \text{ Å})^{-1}$ or $(2000 \text{ Å})^{-1}$. It is interesting to note that in these wires the grain size of Nb$_3$Sn is $\approx 400 \text{ Å}$ and yet the best fit for the straight line was obtained when $1/\sqrt{\rho}$ was approximately twice as large as the grain size. This may imply that only about half of the grain boundaries are effective in pinning the flux lines. (It is well established that grain boundaries are the primary flux-pinning sites in Nb$_3$Sn. See below.)
The second category of results in which plotting $J_c^{1/2} H^{1/4}$ versus $H$ does not yield a simple linear plot is illustrated by the behavior of bronze-processed $Nb_3Sn$ wires which were made with a Ga-containing matrix ($Cu-Sn-Ga$). Representative examples of $J_c^{1/2} H^{1/4}$ versus $H$ plots for these wires are shown in Fig. 36. In this figure, data from Sekine and Tachikawa are also included. It is speculated that the deviation from linearity for these wires is due to the paramagnetic limit on $H_{c2}$ as in $V_3Ga$, in which case, the conditions for which Kramer derived the scaling law do not apply.

The examples cited above, Figs. 34 and 35 appear to indicate that the Kramer scaling law adequately describes the effect on $J_c(H)$ at high fields of variations in the grain size of $Nb_3Sn$. However, an experiment on the anisotropy of $J_c$ casts doubt on this conclusion. As shown in Fig. 37, Tanaka et al. reported the observation of very large differences in $J_c$ of bronze-processed $V_3Ga$ tapes which are measured with applied fields parallel ($J_{cP}$) and perpendicular ($J_{cL}$) to the surface of the tape. These differences are a factor of two or more, depending on the heat treatments and the value of $H$, and they are attributed to the columnar structure of $V_3Ga$ grains which grow perpendicular to the substrate. Thus, the effective grain size with $H$ perpendicular to the tape is smaller than that with $H$ parallel. The difference in $J_c$ was accounted for by taking into account the variation in the effective grain size and assuming that $J_c$ is inversely proportional to the grain size. The Kramer scaling law cannot be applied to these results because of paramagnetic limitation in $V_3Ga$. However, such an experiment for $Nb_3Sn$ is revealing and was performed for $Nb_3Sn$ using a flattened wire which had a matrix-to-core ratio of ~15. Pieces of the wire were heated for 32 h at 725°C and 4 h at 775°C. In both specimens, the $J_c^{1/2} H^{1/4}$ versus $H$ plots are straight in the field range of ~5 to ~10 tesla regardless of the orientation of $H$ to the
tape surface, as shown in Fig. 38. As found by Tanaka et al., \( J_{cL} \) is larger than \( J_{cW} \), but only by 30 to 40%. These smaller differences in \( J_c \) are probably due to nearly equiaxed growth of \( \text{Nb}_{3}\text{Sn} \) grains in these specimens, as observed with a scanning electron microscope. However, these results clearly reveal a difficulty with Eq. (18) as a description of the grain-size dependence of \( J_c \). Variations of \( J_c \) by as much as 30-40% caused by anisotropy in the grain size imply, in Eq. (18), that the \( a_0\sqrt{\rho} \) term must be large enough that a plot of \( J_c^{1/2} H^{1/4} \) versus \( H \) would exhibit an easily observable concave-up curvature, as in Fig. 34. Yet, as seen in the figure, the results show no such curvature and imply that \( a_0\sqrt{\rho} \ll 1 \), in which case variations in \( a_0\sqrt{\rho} \) would cause a negligible variation in \( J_c \). Clearly there is a contradiction here, and its resolution is not obvious at present. Anisotropy in \( H_{c2} \) (and thus \( \kappa_1 \)) with crystallographic orientation is not likely to be the origin of anisotropy in \( J_c \), since, as seen in Fig. 38, the extrapolated \( H_{c2} \) from \( J_{cL} \) and \( J_{cW} \) is essentially the same in both cases. Unfortunately, the values of \( H_{c2} \) for these tapes are significantly lower than those for \( \text{Nb}_{3}\text{Sn} \) wires with the same matrix-to-core ratio. The cause for the reduction of \( H_{c2} \) is not understood at this time. However, we believe that the observed differences in \( J_{cL} \) and \( J_{cW} \) and our conclusion about the scaling law drawn from the present data are valid in spite of the unexplained reduction in \( H_{c2} \) of these specimens.

As a further test of the scaling law, the behavior of the values of \( \kappa_1 \), as determined by Eq. (18) from the slope of \( J_c^{1/2} H^{1/4} \) versus \( H \) plot, were studied for a set of monofilamentary wires which are heat treated for 6, 16, and 64 h at 725°C and 96 h at 675°C. The ratio of bronze-to-core for these wires was \( \approx 7.6 \). The data are plotted in Fig. 39 as \( J_c^{1/2} H^{1/4} \) versus \( H \), and the lack of concave-up curvature over the field range 8-15 tesla implies that \( a_0\sqrt{\rho} \ll 1 \). Values of \( \kappa_1 \) obtained from the slopes of these plots, as suggested
by Eq. (18), are listed in Table 2. (The data from this set of specimens were chosen as an illustration, but essentially identical behavior was observed for wires with other bronze-to-core ratios.) The values of $\kappa_1$ so obtained are smaller than that expected for Nb$_3$Sn, for which the smallest expected value is $\sim$20 for very clean specimens. A quantitative discrepancy of this order is perhaps not unreasonable considering the uncertainty in the value of the shear constant, $C_{66}$, for the flux line lattice which was used in the derivation of Eq. (18). What is a more serious difficulty is the fact that the observed value of $\kappa_1$ increases with heat-treatment time while the observed value of $(H_{c2}/T_C)$ is unchanged (see Table 2). This difficulty is best illustrated by examining the relationship between $(H_{c2}/T_C)$ and $\kappa_1$: 

$$
\frac{H_{c2}}{T_C} = c[N(O)(1+\lambda)]^{1/2}(1-t^2)\kappa_1 = c'\gamma^{1/2}(1-t^2)\kappa_1
$$

(19)

where $c$ and $c'$ are numerical constants, $N(O)$ is the density of states at the Fermi level, $\lambda$ is the electron-phonon coupling constant, $\gamma$ is the electronic specific heat coefficient and $t = T/T_C$. Recent experimental studies of the effect of disorder and nonstoichiometry on the superconducting properties of a variety of A15 compounds show $N(O)$, $\lambda$, and $\gamma$ to be monotonically increasing functions of $T_C$. Our data, Table 2, clearly show that $T_C$ increases by $\sim$4% on increasing the reaction time from 6 h to 64 h at 725°C. Thus one would expect, on the basis of the experimental results cited above, that $N(O)$, $\lambda$, etc. would increase by roughly the same amount. Since our data show $H_{c2}/T_C$ to increase by about 3%, one would then expect $\kappa_1$ to remain more-or-less constant, yet, as seen from Table 1, the value of $\kappa_1$ deduced with the scaling law increases by $\sim$50%! This discrepancy suggests that even though the form of the
scaling law for flux pinning at high fields derived by Kramer seems to be obeyed for Nb\textsubscript{3}Sn, the interpretation of parameters such as "\(k_1\)" which appears in it may not be the same as assumed in Kramer's derivation.

In spite of such serious problems with the scaling law in determining values of \(k_1\) and in accounting for \(J_c\) changes with grain size as described above, it should be pointed out that the trend in variation of \(k_1\) as determined from Eq. (18) is qualitatively correct with regard to changes in \(k_1\) with alloying and irradiation by high energy neutrons of Nb\textsubscript{3}Sn wires. For example, when Nb\textsubscript{3}Sn was alloyed with Ta by using (Nb-Ta) alloy cores rather than pure Nb cores, the slopes of \((J_c^{1/2}H^{-1/4})\) versus \(H\) plots decreased with increased Ta in the compound.\textsuperscript{70} (See Fig. 40.) Also, a similar change in \(k_1\) or \(\Delta(J_c^{1/2}H^{-1/4})/\Delta H\) was observed with increasing neutron fluence when Nb\textsubscript{3}Sn wires were irradiated with neutrons (\(E > 1\) MeV) at ambient temperature.\textsuperscript{131} In both of these cases, it is expected that the normal resistivity increased with alloying or irradiation, thus increasing the value of \(k_1\) or decreasing the slope in \(J_c^{1/2}H^{-1/4}\) versus \(H\) plots. Therefore, in these cases, the trend in \(k_1\) determined by Eq. (18) is as one expects in Nb\textsubscript{3}Sn.

At low fields the critical current is determined by flux motion due to unpinning rather than by shear of the flux-line lattice as for the high-field regime as mentioned above, and thus the density and size of crystal defects in these superconductors will determine \(J_c\). Although a large number of studies have been made on grain-boundary densities (primary defects in these compounds) related to \(J_c\) (see the next section), rarely are the results compared with the scaling law (Eq. 17). In one case, \(J_cH\) for a bronze-processed Nb\textsubscript{3}Sn wire and tape was plotted against \(H^{1/2}(1-h)^{-2}\), and it was found that both data fitted the predicted field dependence well.\textsuperscript{116} However, in these cases, \(H_{c2}=22\) T was assumed, and these values appear to be significantly higher than those values which we now know to obtain for similar wires. Thus, a critical
examination of the scaling law in the low-field regime is still missing.

2. **Temperature Dependence** - Now turning attention to the temperature dependence of the pinning strength $J_cH$ or $J_c$, the variations in these values with temperature for these wires are briefly summarized. The temperature dependence of $J_c$ has a very practical significance since these wires are in some cases designed to be used at higher temperatures than 4.2 K. Also, such measurements can be used for a study of the scaling law; as derived by Kramer, $J_cH$ is proportional to $H_{c2}^{5/2}(T)$ in both high- and low-field regions.

The first measurements of $J_c(T)$ for Nb$_3$Sn and V$_3$Ga multifilamentary wires were made by Crow and Suenaga and the results are shown in Figs. 41 and 42, respectively. More recently, similar measurements were performed on fine multifilamentary wires and their results are essentially the same as shown in these figures. Two aspects of these figures should be noted: 1) $J_c$ varies linearly with $-T$ in most of the temperature region for both wires, and 2) the deviation of the linearity near $T_c$ is more significant in Nb$_3$Sn than in V$_3$Ga. In order to discuss why we expect a linear temperature dependence for $J_c(T)$, we have to go back to the early stages of development of understanding in critical currents for type-II superconductors. According to the critical-state model which was put forth by Anderson and Kim, the critical current is defined from supposing that the critical parameter such as the voltage across a wire is simply represented as the point at which the rate of the flux motion, $R'$, becomes measurable in a given experiment. The rate is given by

$$R' = \omega_o \exp(-F_b/kT) \tag{20}$$

where $\omega_o$ is a vibrational frequency of the flux bundle and

$$F_b = F_p - JH\lambda^2 \xi_o \tag{21}$$
where $F_p$ is the pinning energy, $\lambda$ is the length of the flux line which the force is acting on, and $\lambda$ and $\xi_0$ are the penetration depth and the coherence distance, respectively. At a measurable critical rate $R_c'$,

$$kT \ln \left( \frac{R_c}{\omega_0} \right) = -(F_p)_{\text{critical}}$$

or

$$J_c = \left[ F_p - kT \ln \left( \frac{R_c}{\omega_0} \right) \right] (\frac{H}{\lambda^2 \xi_0})^{-1}.$$  \hspace{1cm} (22a)

Thus, for a small temperature range $J_c$ is expected to decrease linearly with the temperature as observed in Figs. 40 and 41.

The deviation of $J_c(T)$ from the linearity near $T_c(H)$ is thought to be again a consequence of inhomogeneities in the compressional strain from the matrix on the superconductors. As shown earlier, the effect of the strain is more dramatic in $\text{Nb}_3\text{Sn}$ than in $\text{V}_3\text{Ga}$. Thus, this deviation is significantly larger in $\text{Nb}_3\text{Sn}$ as in the case of $J_c^{1/2}H^{1/4}$ versus $H$ plots when the compressional strains in the wires lead to deviations from a linear plot near $H_{c2}$.

The temperature dependence of the pinning force in $\text{Nb}_3\text{Sn}$ monofilamentary wires were critically examined by Schauer and Zimermann and Kroeger et al. They have found that the scaling law as developed by Kramer was not obeyed in these wires in many cases although in some cases the temperature dependence of the pinning force followed Eqs. (16) and (17). Furthermore, Kroeger et al. concluded from their study that microstructural changes are taking place in $\text{Nb}_3\text{Sn}$ due to strain. However, in both of these studies, the method of determination for $H_{c2}(T)$ could be questioned since the onset of a small resistivity at very small current was used for the $H_{c2}(T)$. Since the question being asked is how the "bulk" pinning force varies with $T$ and $H$, both $T_c$ and $H_{c2}$ should be determined by the extrapolation of the "bulk" pinning force with $T$ and $H$, respectively. As shown above, the plots $J_c$ versus $T$ or $J_c^{1/2}H^{1/4}$ versus $H$ in many cases yield straight lines except near $T_c$ or $H_{c2}$. Thus, the linear
extrapolation from these figures appears more suitable for determinations of $H_{c2}$ and $T_c$ for the pinning studies.

A preliminary result on the measurements of the pinning force for a bronze-processed Nb$_3$Sn wire with a matrix-to-core ratio of $\lambda$15 indicated that the magnetic field dependence of the pinning force, $J_c H$, could be expressed by Eqs. (16) or (18) very well at all temperatures between $T_c$ and 4.2 K. This implies that $J_c H$ scales with temperature in this wire. However, its dependence on $H_{c2}$ was nearly parabolic ($H_{c2}^{2.1}$) rather than $H_{c2}^{5/2}$ as in Eq. (16) again indicating that there is another difficulty with the scaling law as developed by Kramer. $H_{c2}$ in this case was determined using Eq. (18).

3. Grain Size Dependence - As discussed in the previous section, $J_c$ in the low-field regime is determined primarily by flux-pinning-site densities. In the Al5 superconductors produced by the bronze process, it is believed that grain boundaries are the primary pinning centers, and it has been initially shown by Scanlan et al. that $J_c$ in the bronze-processed Nb$_3$Sn is inversely proportional to the grain size. Since then, a number of studies have been carried out to examine the dependence of $J_c$ on the grain size in Nb$_3$Sn and V$_3$Ga and these are summarized in the following.

Comparison of the earlier results on Nb$_3$Sn and V$_3$Ga indicated that the critical-current density for Nb$_3$Sn was smaller by an order of magnitude than for V$_3$Ga at a given grain size. However, Livingston showed that the dependence of $J_c$ on the grain size is essentially identical for Nb$_3$Sn, V$_3$Ga, and V$_3$Si if these are produced in an identical manner as shown in Fig. 43. In spite of the interesting coincidence of $J_c$ dependence on the grain size for these three compounds, it should be noted that the superconducting properties of Nb$_3$Sn and V$_3$Si are very sensitive to compressive nonhydrostatic strains,
while $V_3Ga$ is almost insensitive to the strains and that $J_c$ in $Nb_3Sn$ and $V_3Si$ could have been reduced significantly in the wires which were used for this study. Such difference in $J_c$ can be larger than the scatter in the data in Fig. 43. Thus, the identical dependence of $J_c$ in the grain size for these three compounds could be an experimental coincidence. The effect of the compressive strain on $J_c$ has to be carefully considered for a discussion of the grain-size dependence of $J_c$ in $Nb_3Sn$ or $V_3Si$. If $J_c$ for a thin layer is compared with a thick layer of $Nb_3Sn$ of the same initial wire and the same grain size, $J_c$ for the thin layer would be expected to be smaller since the matrix would be harder due to sufficient Sn remaining in the matrix and can compress the $Nb_3Sn$ and Nb filaments more than if the layer is thick. This effect could cause a rather large scatter in the data for $J_c$ versus (grain size)$^{-1}$ in addition to difficulties in measuring the exact grain sizes and layer thicknesses. Finally, the magnetic field which is chosen to compare the $J_c$ versus grain size for different compounds, should influence the relative values of the slope since the field dependence of $J_c$ for these compounds are significantly different. Thus, the average value for the surface current on each grain boundary of 7.0 A/m (or a flux density drop across each grain boundary of 8.4 gauss) as determined from Fig. 43 may not be a universal number for these compounds.

Another question, which is raised, with a figure of the type in Fig. 43, is "Can the $J_c$ keep increasing with decreasing grain sizes?" A theoretical calculation of flux pinning by the grain boundaries in $Nb_3Sn$ owing to the interaction of the flux-line lattice and the grain boundaries through their strain fields indicated an initial linear increase of critical current density with inverse grain size as observed. Furthermore, it predicted that the current density go through a maximum and decrease with decreasing grain size. There are experimental evidences which indicated that $J_c$ started to decrease
beyond some grain sizes (~500-700 Å) as shown in Fig. 44.100,140,141 However, as pointed out by Livingston,9 the theory predicts a maximum at \( D \sim 5a_0 \) (\( D \) and \( a_0 \) are the grain diameter and the flux lattice spacing) and at 4 T a maximum in \( J_c \) is expected at \( D \sim 1200 \) Å. This difference could be attributed to the possibility that not all grain boundaries are not effective in pinning the flux lines and perhaps only every other one is a strong pinning site. Unfortunately all of these data, which indicate decreasing \( J_c \) as the grains become small, are from the wires heated at very low temperatures (~600°C), thus other superconducting properties could have been lower than those with larger grains as recently shown by Finnemore et al.140 Furthermore, the thickness of the layers is generally small in these wires, and this leads to larger reductions in \( J_c \) as well as \( T_c \) and \( H_c \) due to the compressive strain from the matrix. In the figure, it is also shown that there is no significant difference in the \( J_c \) dependence on grain sizes for fine multifilaments140 and for large filaments.141 Similar data by Shaw142 are not included since the geometry of the wire (the internal bronze) is known to have very large radial strains in the Nb3Sn as discussed earlier.

In spite of these interesting data on the relationship between the grain size and \( J_c \), it is difficult to compare these data with the theories which attempt to predict the grain-size dependence of \( J_c \) in these compounds. The primary reason is that none of the above studies included the measurements of both \( T_c \) and \( H_{c2} \). Furthermore, the influence of the compressive strain on these properties has to be carefully included in the experiment for a meaningful comparison with theories or with different data for the relationship in addition to measurements of \( T_c \) and \( H_{c2} \).

4. Effects of Heat Treatments and Alloying - The superconducting critical current density is, as discussed in the previous section, structure sensitive and thus heat-treating conditions and impurities or alloying elements
can influence the values of $J_c$ significantly. In the following, the effects of heat treatment on $J_c$ of Nb$_3$Sn and V$_3$Ga are first summarized and changes in $J_c$ due to alloying of these compounds are then discussed. Also, when it is appropriate, changes in $H_{c2}$ are related to changes in $J_c$ due to metallurgical treatments.

In discussing variations in $J_c$ with heat treatment, changes in three parameters, $T_c$, $H_{c2}$, and the grain size, are of primary concern. In general, for heat treatments of Nb$_3$Sn which were performed between 650°C and 800°C, $T_c$ and $H_{c2}$ increase with heating time until the maximum values for these parameters are reached. For a given thickness of Nb$_3$Sn (>2-3 μm), the heat-treating temperatures do not affect the $T_c$ nor $H_{c2}$ significantly (see Table 2). However, the grain size is a function of both temperature and time of heat treatment. Normally, the lower and shorter the temperature and time, respectively, the smaller the grains are in these compounds. Thus, for Nb$_3$Sn compound layers thicker than (2-3 μm), the primary influence of heat-treating conditions on $J_c$ is due to variations in grain sizes; e.g. $J_c$ at low fields (up to ~12 T) tends to decrease with increasing heat-treating temperature or time as shown by many investigators. In fact, in two cases,\textsuperscript{56,71} it was observed that a relationship between $J_c$ and the thickness was described by $J_c \propto e^{-nd}$ where $n$ (cm$^{-1}$) is independent of time but dependent on temperature and $d$ is the thickness of Nb$_3$Sn layers. $n$ increased with temperature due to faster growth of grains at higher temperature than at low temperatures. However, the $e^{-nd}$ dependence, appeared to be applicable only in the case where depletion of Sn in the matrix is a factor\textsuperscript{56} for the growth of the layer. Also, in Fig. 19, the dependence of $J_c$ at 6.5 T on the reaction temperature is shown\textsuperscript{58} and such a drastic decrease in $J_c$ of Nb$_3$Sn with the temperature is a reflection of the larger Nb$_3$Sn grains at the high reaction temperatures as shown in Fig. 22.
Similar decreases in $J_c$ of $\gamma$ Ga due to high reaction temperatures were also observed.\(^{13,61}\) At the very high-magnetic fields, ($H > 12$ T), $J_c$ normally increased with temperature (below 750°C) and time.\(^{14,56,143}\) (Also see Fig. 39.) This is caused by increases in the value of $H_{c2}$ and there are two possible reasons for increases in $H_{c2}$. They are increases in $T_c$ due to the increased ordering of $\text{Nb}_3\text{Sn}$ and to the decrease in the compressive strain in the layer since the matrix becomes softer as Sn in the matrix is decreased.

In discussing effects of alloying additions to the core and/or the matrix on $J_c$ and $H_{c2}$, it is helpful to consider three types of alloying-induced changes in physical properties which can influence critical current densities and magnetic fields of Al5 superconductors. They are a) the normal state resistivity $\rho_N$, b) the critical temperature and c) grain sizes. $\rho_N$ and $T_c$ influence $H_{c2}$ of the wires, thus $J_c$ at very high fields. The grain size is particularly important in determining $J_c$ at lower fields. But as shown earlier, $J_c$ at high fields depends on the grain sizes, also. The influences of $\rho_N$ and $T_c$ on $J_c$ at low fields are not clear at the present time. As discussed in the section on $T_c$, a very large number of elements have been added to either or both the core or/and the matrix. In the following, each addition will be discussed in reference to variations in the above physical properties of the compounds and their influence on $J_c$ and $H_{c2}$.

For $\text{Nb}_3\text{Sn}$, transition element additions Ti,\(^{144}\) Zr,\(^{56,80}\) Hf,\(^{80}\) and Ta\(^{70,81}\) to the Nb core have been extensively studied for their effects on superconducting properties, primarily $J_c$. In particular, the addition of Ta was of great interest because Ta alloys with Nb without changing the workability of the alloy from that of Nb, implying that the fabrication method for $\text{Nb}_3\text{Sn}$ fine filamentary wires with a Nb-Ta alloy will not need to be changed from that which uses pure Nb rods. The study of Ta addition\(^{70}\) to the core using
monofilamentary wires indicated that the addition decreased $T_c$ (see fig. 33) but increased $H_{c2}$ as shown in Fig. 45. This increase in $H_{c2}$ is thought to be due to an increase in $\rho_N$. As shown in Fig. 46, the increase in $H_{c2}$ with the addition of Ta up to 10 wt% Ta in Nb was found to increase the value of $J_c$ for alloyed Nb$_3$Sn from the value of $J_c$ for the unalloyed Nb$_3$Sn at 16 T but to slightly decrease at 10 T. But the addition of 20 wt% Ta decreased the value of $J_c$ to nearly that of the unalloyed Nb$_3$Sn at 16 T and significantly decreased below the value of the unalloyed wire at 10 T. Observations of the grains in these wires with a scanning electron microscope indicated that there was no observable difference in the size of the grains between the Nb$_3$Sn and (Nb-Ta)$_3$Sn compound layers. $J_c$ at magnetic fields below ~10 T decreased monotonically with increasing amounts of Ta in the core. Thus, increasing the value of $H_{c2}$ without significant reductions in $T_c$ can increase $J_c$ at very high magnetic fields, but critical currents at low fields ($H<10$) generally decreased with increased $H_{c2}$ by alloying.

The additions of Ti, Zr, and Hf could decrease $T_c$ if significant quantities of these elements are incorporated in Nb$_3$Sn. However, the ranges of compositions in the alloyed core which were investigated were limited to less than 5 at.%, and the change in $T_c$ by these additions was found to be small. In one case, it was found that $T_c$ of Nb$_3$Sn with Hf additions slightly increased with the Hf content in the core. The primary effects of the addition of these elements are in the reduction of the grain size and increases in $H_{c2}$, presumably through increased $\rho_N$. These additions were also found to limit the grain growth in Nb$_3$Sn. The first indication of reduced grain growth with Zr addition was shown by Suenaga et al. When $J_c$ versus thickness was plotted for the early Nb$_3$Sn wires, the rate of the decrease in $J_c$ with increasing thickness was slower with Zr in the core than in pure Nb$_3$Sn. This suggests that the grain growth is limited by the presence of Zr in the layer, possibly at
the grain boundary. At the same time the growth of the compound was also faster with Zr again indicating smaller grains for faster diffusion for Sn through grain boundaries. Also, $H_{c2}$ is increased with Zr additions to the core and $J_c$ at very high magnetic fields ($H>12$) was again increased over the value of the unalloyed wires. Similar observations were also made for additions of Ti and Hf (Fig. 44). Furthermore, as in the case of Ta addition, increased Ti and Hf additions beyond a small amount of these elements were found to decrease $J_c$ at all fields except at very high fields (near $H_{c2}$) in spite of increasing $H_{c2}$.

As mentioned earlier, the addition of Mg (0.5 at.%) to the bronze matrix has the most dramatic effect on the grain sizes and the growth of $\alpha$-$\beta$-$\gamma$Sn as shown by Togano et al. However, what is very puzzling is that $J_c$ measured at 6.5 T did not vary significantly with the addition in spite of an at least fivefold difference in grain sizes for the wires which were heated at 800°C as shown in Fig. 19. In fact, a drop in $J_c$ by a factor of $\sim$2.5 was observed when the wire contained 0.5 at.% Mg in the matrix and was heated for 100 h at 700°C. The grain sizes for these wires were noted to be approximately the same. Unfortunately, the measurements of $J_c$ were only reported for 6.5 T, and we do not know how $J_c$ for the unalloyed and alloyed wires compare at very high fields. However, since $T_c$ for Mg alloyed wires were not significantly different, there appear to exist some unknown effects leading to a reduction of $J_c$ for a given grain size with the Mg addition in the matrix without it being incorporated in the Al5 structure. Finally, although the growth rate and the relative values of $J_c$ increased with the Mg addition for the wires heat treated above 750°C, $J_c$ for these wires was still lower than the unalloyed wire which was heated at 700°C (Fig. 19). Thus, the practical use of such an addition for multifilamentary wires appears not to be of any significance (at least for the medium magnetic field range).
A small amount of Sn can be added to the Nb core without making the alloy excessively hard for cold drawing. It was found that the addition was effective in increasing the Nb₃Sn layer growth rate and increased Jₓ at 4 T, probably due to refinement of the grains.⁶⁶

Both additions of Al⁶⁷ and Zn⁷⁵ to the matrix in some cases increased the layer growth rate, but Jₓ in both wires were always lower than that for the wire with the pure bronze matrix (Cu-7 at.% Sn). Also, both of these elements were known not to be incorporated in the compound. But when Al was added to both the core and the matrix, Al was incorporated in the compound and Jₓ at high magnetic fields increased above that for the unalloyed wire.⁶⁷

Finally, as mentioned previously, the addition of Ga to the matrix has been found to increase Tₙ and Hₙ₂ of Nb₃Sn.⁸⁰,⁸³ (See Table 1 for example.) In this case, Ga is incorporated in the Al₅ structure, probably at Sn sites. However, the growth rate of the compound was considerably slowed by the addition and the grain size of Nb₃(SnGa) increased significantly over that for pure Nb₃Sn, thus resulting in a reduction of Jₓ from the value of Jₓ for the unalloyed wires except at very high magnetic fields (Fig. 4). The use of alloyed Nb cores with Zr and Hf in conjunction with the matrix increased the growth rate and Jₓ of Nb₃Sn increased by considerable amounts over the value for the wire with the Cu-Sn-Ga matrix. The observed increases in high field Jₓ appear to be due to increased Hₙ₂ by the incorporation of Ga and Zr or Hf in Nb₃Sn. (See Table 1.) An interesting aspect of the Ga addition to Nb₃Sn with respect to the magnetic field dependence of Jₓ is pointed out in the previous section that Jₓ does not follow a h¹/² (1-h)² dependence while essentially all other data of Jₓ for Nb₃Sn follow this dependence. (See Fig. 36.)

In spite of the observed significant increases in Jₓ at high fields and in Jₓ of Nb₃Sn with Ga and Zr or Hf additions to the matrix and the core, the technological values of the additions appeared to be limited to the external
diffusion processed multifilamentary wires. The reason is that the amount of Sn in the matrix has to be greatly decreased to avoid precipitates in the matrix or excessively high work hardening rate for the matrix. (See Table 1.) When the external diffusion method is used, Ga can be added externally thus avoiding the above difficulty. The additions of Zr or Hf in the Nb core may also cause fabrication difficulties due to higher-yield stresses and work-hardening rates during the extrusion and drawing processes while additions of Ti to the Nb core will keep the drawability of the filaments for technologically meaningful multifilamentary wires. Also, Nb-Ti alloys are considerably easier to melt than Nb-Ta alloys. It appears that small additions of Ti (~2 at.%) to the core appear to produce Nb$_3$Sn with $J_c$ nearly as high as that for Ta alloyed wires.

In contrast to the study of Nb$_3$Sn, a relatively smaller number of elemental additions to V$_3$Ga wires were investigated. Al, Mg, and Mn were added to the matrix while Al, Ga, and Ti were alloyed with V for the core materials. As shown in Fig. 21, the effect of aluminum additions to the Cu-Ga matrix while keeping the (Al+Ga) content constant at 20 at.% is to increase $H_{c2}$ and to keep $T_c$ unchanged up to 2 at.% Al. On further additions of Al, both $T_c$ and $H_{c2}$ decreased. The associated change in $J_c$ at 6.5 T is an increase in $J_c$ by a factor of two for Al additions of 2 to 8 at.%. This increase is understood as a manifestation of decreased grain size. At very high fields, $J_c$ of V$_3$Ga wires decreased with alloying beyond 2 at.% Al, probably due to decreased $H_{c2}$ and $T_c$. The addition of Al to the V core also resulted in comparable $J_c$ for V$_3$Ga in these wires as in the case of the combined addition of Ga in the core and Mg in the matrix discussed below. However, again, the addition of 10 at.% Al in V will probably make the large scale fabrication of multifilamentary wires very difficult due to the increased work-hardening rate of the V-Al alloy.
As in the case of Nb$_3$Sn, a small addition of Mg to the matrix dramatically increased the growth rate of V$_3$Ga (see Fig. 20) and increased $J_c$ significantly. The addition of Ga to the core also increased the growth rate and $J_c$. However, the most pronounced increase in $J_c$ was observed when 0.5 at.% Ga was added to the core and 0.5 at.% Mg was added to the matrix simultaneously. Although the growth rate did not increase significantly over that of the composite with only 0.5 at.% Mg addition to the matrix, $J_c$ at 9.5 T increased by 2.5 times by the combined use of Ga in the core and Mg in the matrix. $J_c$ for this wire is also approximately 4 times larger than $J_c$ for the unalloyed V$_3$Ga. Since $T_c$ nor $H_{c2}$ increased only slightly, the increased $J_c$ by these alloying were attributed to the refined grains by the additions. However, it is interesting to note that the combined addition of Ga to the core and Mg to the matrix increased the growth rate by only a small fraction implying that the grain sizes also decrease by a small amount. Then, it is difficult to attribute the increase of $J_c$ solely to the grain refinement when there is a factor of 2.5 increase in $J_c$ without significant grain size reduction.

The highest critical current density for Al5 superconductors were, however, achieved in V$_3$Ga which was formed in a composite of a (V-9.5 at.% Ga) core and a (Cu-17.5 at.% Ga) matrix. $J_c$ at 15 T was $3 \times 10^5$ A/cm$^2$ for a 2.5 µm thick layer. Although the addition of Ga to the V core is very attractive in producing very high critical currents, fabrication of commercial scale multifilamentary wires has experienced difficulties in preparation of a core alloy which is sufficiently ductile for the extrusion and drawing processes with the bronze.

A small addition (0.5 at.%) of Mn is also known to increase the growth rate and the critical current density of V$_3$Ga due to refinement of the grains. But, $J_c$ in these wires were substantially lower than those discussed above.
5. What is Required for High $J_c$? - In this section, several aspects of the relationship between magnetic field dependence of critical-current densities in the $\text{Nb}_3\text{Sn}$ and $\text{V}_3\text{Ga}$ wires and metallurgical treatments are summarized. First, we will restate important observations regarding the $J_c$ of $\text{Nb}_3\text{Sn}$ wires:

a) In most cases, $HJ_c \sim h^{1/2}(1-h)^2$ is obeyed in the high-field region. For very small grain sizes, $HJ_c \sim h^{1/2}(1-h)^2(1-a\sqrt{\rho})^2$ is obeyed if a proper value for $\sqrt{\rho}$ is chosen.

b) Upon increasing the heat-treatment time or temperature, the slope of the plot $J_c^{1/2}H^{1/4}$ vs $H$ decreases, thus $J_c$ decreases.

c) On alloying, $H_{c2}$ increases, but the slope decreases. Thus $J_c$ decreases except at very high magnetic fields ($H>16 \text{T}$).

d) Variations in $H_{c2}$ caused by the compressive strains did not change the slope significantly. Presumably, $H_{c2}$ is changed due to the same factors which cause the changes in $T_c$ (and thus $H_c$).

e) In the high field region, the grain size strongly influences $J_c$ in contrast to the predictions of Kramer's Scaling law.

Based on these observations, one might speculate a relationship between the critical current, magnetic field, and pinning site density to be of the form:

$$J_c^{1/2}H^{1/4} = f(\sqrt{\rho}, \kappa_1) \frac{(H_{c2} - H)}{(1-a\sqrt{\rho})}$$

where $f$ is a function of the pinning site density and $\kappa_1$. Existing experimental data\(^{(97,70)}\) and the Kramer's equation suggest that an approximate form of $f$ may be:

$$f = A' \rho^{1/4}/\kappa_1$$

where $A'$ is a function of the pinning strength. Then, the expression for the pinning force will be
\[ J_C H = \frac{A \rho^{1/2} (H_{c2} - H)^2 H^{1/2}}{\kappa_1 (1 - a_0 \sqrt{\rho})^2} \]  

(25)

where \( A = A' \). It is very instructive, as pointed out by D. O. Welch,\textsuperscript{147} to examine the influence of variations in individual parameters in Eq. (25) on \( J_C \) by differentiating Eq. (25) with respect to these parameters as

\[ \frac{\Delta J_C}{J_C} = \frac{1}{n} \left[ \frac{1 + a_0 \sqrt{\rho}}{1 - a_0 \sqrt{\rho}} \right] \frac{\Delta \rho}{\rho} + \frac{2 H_{c2}^2 H}{H_{c2}^2 - H} \frac{\Delta H_{c2}}{H_{c2}} + \frac{2 H_{c2}}{H_{c2}^2 - H} \frac{\Delta \kappa_1}{\kappa_1} + \frac{\Delta A}{A} \]  

(26)

A particularly interesting aspect of Eq. (26) is that the change in \( J_C \) due only to \( \kappa_1 \) cannot produce the crossing behavior in the plot, \( J_C H^{1/4} \) vs \( H \), as shown in Fig. 40 with alloying Ta in the core. If the dependence of \( f \) on \( \kappa_1 \) is \( \kappa_1^n \) where \( n > 1 \), then, the equation will contain the crossing behavior with increasing \( \kappa_1 \). However, this results in the crossing field to be constant for a given \( n \) and the result shown in Fig. 40 indicates that the crossing field can vary significantly. Thus, for this particular choice of \( f(\sqrt{\rho}, \kappa_1) \) the large decrease in the slope, which was observed in Fig. 40 with the Ta addition, could be associated with variation in other parameters in addition to \( \kappa_1 \). Observation of the grain sizes with a scanning electron microscope noted that there was no noticeable change in the grain sizes with the Ta alloying of the cores. Furthermore, \( T_c \) decreased only 10% at the 20 wt% Ta in the core. Thus, the likely cause for the large reduction in the slope of the \( J_C H^{1/4} \) vs \( H \) plot is suspected to be due to the reduction of the pinning strength, \( \Delta A \) in Eq. (26), and as pointed out earlier (Section IV-C-4), reductions in the pinning strength by alloying of the compounds have been observed.

Then, in order to achieve high-current densities at intermediate magnetic fields (8\( \leq H \leq 16 \) T) which is a region in magnetic fields of interest for many applications, Eq. (25) requires small grain sizes and high-critical magnetic
fields. But the means of producing fine grained Nb$_3$Sn and of achieving high $H_{c2}$ need to be carefully chosen. As discussed earlier, when the fine grain size is achieved by alloying and the alloying elements are contained at the grain boundary, the flux-pinning strength of the boundary could be reduced significantly from the value for the pure boundary.

In the case of the V$_3$Ga wires, it is difficult to use the equations such as Eq. (18) or Eq. (25) since the experimentally measured $H_{c2}$ is paramagnetically limited, and it is very difficult to extrapolate the GLAG $H_{c2}$ accurately since this $H_{c2}$ is very high ($\approx 30$ T). However, it is hoped that the above conclusions for Nb$_3$Sn can be qualitatively extended to the behavior of $J_c$ in the V$_3$Ga wires.

V. Future Directions

Some questions, which were raised in the previous sections and which are considered to be of primary importance, are briefly summarized in this section. In the area of the compound growth kinetics, the concept of the grain-boundary diffusion for the growth appeared to be qualitatively correct, but a quantitative examination of the growth with accurate data on compositional profiles of the layer is yet to be made. A clarification of the role that impurities play in the compound growth is badly needed. In particular, the location of impurities in the compound needs to be determined in relationship to impurity pinning of the grain boundary for grain growth. The influence of Sn and Ga activities on the grain-boundary diffusion also requires more detailed consideration. Furthermore, the mechanism for the void formation at the Nb$_3$Sn-bronze interface needs to be quantitatively examined.

In the area of $T_c$, one of the most interesting problems is understanding the influence of alloying in Al5 compounds on the strain sensitivity and on the related softening and hardening of Young's modulus in these compounds with decreasing temperature. It is possible to take an advantage of these
variations to improve the critical properties of the composite wires by minimizing the degradation due to the precompression of the compound through the differential thermal expansion coefficient. Another important problem is the determination of the dependence of \( T_c \) on the reaction temperature. In regard to \( J_c \), a theory for the flux pinning is one of the most important needs as mentioned above in particular, there is no attempt to theoretically describe flux pinning in paramagnetically limited superconductors. Experimental and theoretical studies for effects of impurities on the grain boundary flux pinning, especially at the high-field region are needed. Further studies of temperature dependence of \( J_c \) and \( H_{c2} \) related to the scaling are still required.

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REFERENCES


23. Y. Hashimoto, private communication.


34. See for a review the article by R. Roberge in this Proceedings.
42. T. S. Luhman, O. Horigami, and D. Dew-Hughes, Appl. Polymer Symp. 29, 61 (1971).
46. J. D. Livingston, M. of Mat'l. Sci. 12, 1759 (1977).
63. D. O. Welch, private communication.
64. Unpublished.
65. D. Smathers and D. C. Larbalestier, to be published in Adv. in Cryo. Engin., Vol. 26; to be published in Proc. of Conf. on Multifilamentary Al5 Superconductors, Brookhaven National Laboratory, Upton, NY (May 1980).
73. Unpublished.
74. R. M. Scanlan, private communication.
76. Unpublished.
85. T. S. Luhman, unpublished.


111. K. Aihara, unpublished work.


115. J. D. Livingston and R. M. Scanlan, unpublished work.


131. C. L. Sneed, Jr., unpublished.


137. Unpublished.


144. Unpublished.

146. D. G. Howe, private communication.

147. D. O. Welch, private communication.
Table 1

Heat treatment condition $T_c$ and $H_{c2}$ (4.2 K) for the composite tape specimens. $H_{c2}$ (4.2 K) is defined as a field where $J_c$ is equal to $2 \times 10^3$ A/cm$^2$.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Heat treatment ($^\circ$Cxh)</th>
<th>$T_c$ (K)</th>
<th>$H_{c2}$ (4.2 K) (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Nb/7 Sn</td>
<td>800 x 100</td>
<td>17.1</td>
<td>17</td>
</tr>
<tr>
<td>B: 2 Zr/7 Sn</td>
<td>800 x 100</td>
<td>17.3</td>
<td>17.5</td>
</tr>
<tr>
<td>C: 2 Hf/7 Sn</td>
<td>800 x 100</td>
<td>17.5</td>
<td>19</td>
</tr>
<tr>
<td>D: 5 Hf/7 Sn</td>
<td>800 x 100</td>
<td>17.6</td>
<td>21</td>
</tr>
<tr>
<td>E: 2 Hf/5 Sn-4 Ga</td>
<td>800 x 100</td>
<td>17.7</td>
<td>$\sim$22</td>
</tr>
<tr>
<td>F: 5 Hf/5 Sn-4 Ga</td>
<td>800 x 20</td>
<td>17.7</td>
<td>$\sim$21.5</td>
</tr>
<tr>
<td>G: Nb/3 Sn-9 Ga</td>
<td>800 x 100</td>
<td>17.6</td>
<td>20</td>
</tr>
<tr>
<td>H: 5 Hf/3 Sn-9 Ga</td>
<td>800 x 20</td>
<td>18.0</td>
<td>$\sim$22.5</td>
</tr>
</tbody>
</table>
Table 2

Superconducting Properties of the Nb3Sn Wires

<table>
<thead>
<tr>
<th>Time</th>
<th>6h/725°C</th>
<th>16h/725°C</th>
<th>64h/725°C</th>
<th>96h/675°C</th>
</tr>
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<tbody>
<tr>
<td>( k_1 )</td>
<td>9.2</td>
<td>9.9</td>
<td>13.8</td>
<td>8.66</td>
</tr>
<tr>
<td>T(_c)(^{(a)})</td>
<td>16.15</td>
<td>16.45</td>
<td>16.85</td>
<td>16.80</td>
</tr>
<tr>
<td>H(_c2)(^{(b)})</td>
<td>16.6</td>
<td>16.9</td>
<td>17.5</td>
<td>17.6</td>
</tr>
</tbody>
</table>

\(^{a}\)The midpoint \( T_c \) measured inductively with the bronze matrix still present.

\(^{b}\)Determined by the linear extrapolation according to Eq. (18).
FIGURE CAPTIONS

Fig. 1. Schematic diagrams for (a) the bronze and (b) the external diffusion processes for multifilamentary $\text{Nb}_3\text{Sn}$ and $\text{V}_3\text{Ga}$ wires.

Fig. 2. Schematic diagrams for formation of $\text{V}_3\text{Ga}$ layers by a diffusion reaction between vanadium and gallium rich compounds for a) without Cu and b) with Cu addition (Ref. 12).

Fig. 3. Schematic diagrams for modified bronze processes a) the internal Sn diffusion, b) the internal bronze, and c) the internal Sn-Nb tubing processes. The dotted and the shaded areas represent the bronze and Sn-Cu eutectic alloys, respectively.

Fig. 4. A schematic diagram for the wrap-process for fabrication of multifilamentary wires.

Fig. 5. The Nb-Sn phase diagram (Ref. 39).

Fig. 6. Part of a section of the Nb-Cu-Sn ternary phase diagram at $\sim 700^\circ\text{C}$ (Refs. 43 and 44).

Fig. 7. Part of a section of the Nb-Ge-Cu phase diagram at $\sim 700^\circ\text{C}$ (Refs. 43 and 44).

Fig. 8. Part of a section of the V-Cu-Si ternary phase diagram at $\sim 700^\circ\text{C}$ (Refs. 44 and 46).

Fig. 9. More detailed parts of sections of a) the Nb-Sn-Cu and b) the V-Ga-Cu ternary phase diagrams.

Fig. 10. A schematic pseudo-binary phase diagram for the Nb-(Cu-Sn) system for the Nb-(Cu-Sn) diffusion couple.

Fig. 11. Schematic diagrams of a) the Sn-concentration and b) the Sn's chemical potential variations in the Nb-$\text{Nb}_3\text{Sn}$-(Cu-Sn) diffusion couple. Dotted lines represent the concentration and the chemical potential in a grain boundary.
Fig. 12. Schematic representation of a Nb$_3$Sn layer containing a grain boundary (Ref. 53).

Fig. 13. Auger Sn depth profiles for Nb$_3$Sn layers which were heated at 650°C (Ref. 65).

Fig. 14. A compositional profile of a Nb$_3$(SnGa) layer indicating an increased concentration of Ga at the Nb-Nb$_3$(SnGa) interface.

Fig. 15. Concentration dependences of the a) Nb$_3$Sn and b) V$_3$Ga growth rates on a) Sn and b) Ga.

Fig. 16. A transmission electron micrograph of Nb$_3$Sn grains growing at a Nb-(Cu-Sn) interface (Ref. 79).

Fig. 17. Scanning electron micrographs of Nb$_3$Sn layers which were formed at the interfaces of a) Nb-(Cu-Sn) and b) Nb-(Cu-Sn-0.5 Mg) at 800°C for 20 h (Ref. 58).

Fig. 18. Nb$_3$Sn layer thickness vs reaction time at 800°C for the composite tape specimens with the various cores and the matrices as listed in Table 1 (Ref. 80).

Fig. 19. Dependence of a) Nb$_3$Sn layer thickness and b) critical current densities at 6.5 Ton heat-treating temperatures for Nb-(Cu-Sn) and Nb-(Cu-Sn-0.5 Mg) tapes (Ref. 58).

Fig. 20. Dependence of V$_3$Ga layer growth rates on reaction temperatures for various composites (Refs. 89-92).

Fig. 21. Critical temperature, magnetic fields, and currents of V$_3$Ga vs Al contents in the bronze (Ref. 91).

Fig. 22. Grain size for bronze-processed A15 compounds as a function of reaction temperature (Ref. 97).

Fig. 23. Variations in $T_c$ of A15 compounds due to compressive strains resulting from differential thermal expansion between the core and the matrix. The ratio of the matrix to the core, $R$, thus the strain, was varied by gradually etching off the matrix.
Fig. 24. Critical-current densities of Nb_3Sn wires with various matrix-to-core ratios as a function of applied magnetic field.

Fig. 25. The ratio of critical fields to critical temperatures of monofilamentary Nb_3Sn wires as a function of the bronze-to-core ratio.

Fig. 26. The difference in T_c without and with the matrix for Nb_3Sn wires as a function of neutron fluence (Ref. 110).

Fig. 27. Critical temperature of monofilamentary Nb_3Sn wires as a function of heat-treatment time at 725°C for the wires a) with the matrix, b) without the matrix, and c) after annealed at 725°C for 1/2 h (Ref. 30).

Fig. 28. Critical temperature of multifilamentary Nb_3Sn wires as a function of heat-treatment time at 725°C for the wires a) with the matrix, b) Cu removed, c) annealed at 725°C for 1/2 h, and d) with the bronze removed (Ref. 30).

Fig. 29. a) Critical temperatures and b) lattice parameters of Nb_3Sn wires as a function of heat-treatment temperature (Ref. 111).

Fig. 30. Critical temperature of bronze-processed V_3Ga tapes as a function of heat-treatment time at 700°C for the tapes with the matrix of different Ga concentrations (Ref. 11).

Fig. 31. Critical temperature of bronze-processed V_3Ga as a function of Ga concentration in the matrix for V_3Ga layer thicknesses of ~1 μm and ~3 μm.

Fig. 32. Critical temperature of bronze-processed V_3Ga as a function of reaction temperature for ~1 and ~2.5 μm thick V_3Ga layers.

Fig. 33. Critical temperature of (Nb,Ta)_3Sn wires with and without the matrix as a function of Ta contents in the Nb-Ta alloy cores (Ref. 102).

Fig. 34. A plot for J_{c1}^{1/2} H_{c2}^{1/4} vs H for a monofilamentary Nb_3Sn wire which was heat treated at 725°C for 120 h indicated the extrapolated H_{c2} and the low current density H_{c2} (Ref. 122).
Fig. 35. A plot for $J_c^{1/2} H^{1/4} (1-a_0/\sqrt{2})$ vs $H$ for a in situ Nb$_3$Sn wire which was heat treated at 550°C for 6 days. This plot shows that the inclusion of $(1-a_0/\sqrt{2})$ with $\sqrt{2} = (10^3 \text{ A})^{-1}$ is necessary to make the plot linear with $H$ (Ref. 122).

Fig. 36. $J_c^{1/2} H^{1/4}$ vs $H$ for Ga-containing Nb$_3$Sn wires. These data do not appear to obey Eq. (18), (Ref. 122).

Fig. 37. Critical current density of a bronze processed V$_3$Ga tapes vs magnetic field for applied field parallel ($J_{cH}$) and perpendicular ($J_{cL}$) to the tape (Ref. 99).

Fig. 38. Plots for $J_c^{1/2} H^{1/4}$ vs $H$ for $H$ parallel ($J_{cH}$) and perpendicular ($J_{cL}$) to the surface of Nb$_3$Sn tapes (Ref. 122).

Fig. 39. Plots for $J_c^{1/2} H^{1/4}$ vs $H$ for a series of Nb$_3$Sn wires which were heat treated for 6, 16, and 64 h at 725°C and for 96 h at 675°C (Ref. 106).

Fig. 40. Plots for $J_c^{1/2} H^{1/4}$ vs $H$ for a series of Nb$_3$Sn wires which the cores were alloyed with Ta (Ref. 31).

Fig. 41. Critical current density vs temperature at various magnetic fields for the Nb$_3$Sn multifilamentary wire.

Fig. 42. Critical current density vs temperature at various magnetic fields for the V$_3$Ga multifilamentary wires.

Fig. 43. Grain size dependence of critical-current densities of bronze-processed Nb$_3$Ga, V$_3$Ga, and V$_3$Si (Ref. 97).

Fig. 44. Critical current density at 4 T vs reciprocal grain size for various bronze-processed Nb$_3$Sn wires (Ref. 140).

Fig. 45. Critical magnetic fields for $(\text{Nb,Ta})_3$Sn wires as a function of the core composition (Nb-Ta), (Ref. 31).

Fig. 46. Critical current density of Nb$_3$Sn tapes with Hf and Ga additions as a function of magnetic fields as indicated in Table 1 (Ref. 80).
FIGURE 1.
FIGURE 3.
FIGURE 5.
FIGURE 6.
FIGURE 7.
2500 °C

α + LIQUID

~ 700 °C

DIFFUSION PATH

α

NbSS + Al5

Nb3Sn (Al5)

Al5 + CuSS

LIQUID + Al5

25

at. % Sn

FIGURE 10.
FIGURE 11.
Multiplexed Sn Auger Peak-to-Peak Height
Arbitrary Units

FIGURE 13.

Sputtering Time

300 min.

300 hr

20 hr

10 hr

5 hr

2 hr

Noise level
(Nb−1 Zr): FILAMENT
(Cu−5 Sn−8.5 Ga): MATRIX
800°C FOR 8 DAYS

\[ \text{MATRX} \quad \text{Nb}_3 (\text{Sn}_{1-x} \text{Ga}_x) \quad \text{Nb} \]

DISTANCE (1 μm/STEP)

FIGURE 14.
Figure 16

Cu-Sn Alloy

$\text{Nb}_3\text{Sn}$

2000 Å

$\text{Nb}$
FIGURE 18.
FIGURE 19.
FIGURE 20.
FIGURE 21.
FIGURE 22.
FIGURE 24.

Br/Nb
- 1.1
△ 3.4
+ 7.6
○ 15
△ 44
96h at 675°C
FIGURE 25.
FIGURE 27.

SINGLE CORE Nb$_3$Sn; $R_v \sim 14$

- (a) as-heat treated, 725 °C
- (b) (a) + Remove Bronze
- (c) (b) + 725 °C, 1/2 h

$T_c$ (K) vs. HEAT TREATING PERIOD (h)
CORRECTED $T_c$ (mid-point) [K]

- (a) as heat treated, 725°C
- (b) + removed Cu
- (c) + 725°C, 1/2 h
- (d) remove bronze

HEAT TREATING PERIOD (h)

FIGURE 28.
LATTICE PARAMETER, $a_0$ (Å) vs. CRITICAL TEMP. (°K)

HEAT TREAT. TEMP. (°C)

FIGURE 29.
FIGURE 30.
FIGURE 31.

Critical Temp. $T_c$(°K) vs (at.% Ga) in the Cu-Ga alloy at 700°C. 

- O TANAKA et al
- △ BERTHEL et al

- ~3 μm
- ~1 μm
(Nb-Ta)$_3$Sn
SINGLE CORE; $R_V \sim 3$

$T_c$ (MID-POINT) [K]

MATRIX WITH; WITHOUT at 725°C

- 16 h
- 64 h
- 120 h

NOMINAL CORE COMPOSITION (wt % Ta)

FIGURE 33.
\[(I_c H)^{1/2} H^{1/4} \quad (A^{1/2} T^{1/4})\]
FIGURE 35.

\[ (1 - \rho^{1/2}a_0) J_C H^{1/4} = \text{(1000 A)}^{-1} \]

\( \rho^{1/2} = 550^\circ \text{C} \) 6 da.

\[ \rho^{1/2} = (1000 \text{Å})^{-1} \]
$J^{1/2} H^{1/4}$ ($\mu A^{1/2} \AA^{-1/4} \text{m}^{-1} \cdot 10^3$)

FIGURE 36.

- Core: Ni, 7 wt% Ti, 90-2 wt% Sn, 6 wt% Ga
- Matrix: Cu, 7.5 wt% Ti, 90-2 wt% Sn, 6 wt% Ga

- 725°C, 120 h
- 775°C, 120 h
- 800°C, 100 h (Semen and Toshikawa)
FIGURE 37.
Figure 38.

\[ J_{c}^{1/2}H^{1/4} \left( 10^{5}A^{1/2}T^{1/4} \text{ m}^{-1} \right) \]

- J_{C11}
- J_{C12}

Points:
- • 775°C, 4h (1.1 μm)
- Δ 725°C, 32h (1.5 μm)
FIGURE 39.

Br/Nb = 7.6

- 96h - 675 C (3.5 μm)
- 06h - 725 C (1.7 μm)
- 15h - 725 C (3.1 μm)
- 64h - 725 C (7.6 μm)

\[(J_c H)^{1/2} H^{-1/4} (10^5 A / 2 T / 4 m)^{-1}\]

H (tesla)
NOMINAL COMPOSITION OF CORES

- Nb
- Nb 3 Ta
- Nb 7 Ta
- Nb 10 Ta
- Nb 20 Ta

HEAT TREATMENT AT 725 °C FOR 64 h

FIGURE 40.
FIGURE 43.
NOMINAL CORE COMPOSITIONS (wt. % Ta in Nb)

HEAT TREATMENTS AT 725 °C
- 16 h
- 64 h
- 120 h

CRITICAL MAGNETIC FIELDS (T)

CORE COMPOSITION (at % Ta in Nb)

FIGURE 45.
FIGURE 46.