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METALLURGY OF CONTINUOUS FILAMENTARY Al₅ SUPERCONDUCTORS

by

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Metallurgy of Continuous Filamentary Al5 Superconductors

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.¹ 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.^{2,3,4} 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^{5,6} and high-energy accelerators⁷ 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. Luhman⁸ and J. D. Livingston.⁹

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, 1969. 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 Al5 compounds such as Nb_3Sn . 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_3Sn 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_3Ga tapes in Japan, also realized that V_3Ga could be formed by a solid-state reaction at the interface between V and (Cu-Ga) and the produced V_3Ga 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 Al5 superconductors, primarily V_3Ga tapes. One of their early contributions to the fabrication of Al5 conductors was to produce a V_3Ga 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 800°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.%).^{9,10} 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.³ 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 Sampson¹³ 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 "bronze 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 "bronze process" are discussed, a very important contribution by the Harwell group

in the development of multifilamentary Al₅ wires has to be mentioned.¹⁴ 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.¹⁵ 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 Sampson¹⁶ soon after the discovery of the original "bronze process" following a suggestion to increase thickness of the layer in the bronze-processed V₃Ga 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 Nb₃Sn multifilamentary wires without being aware of the work at BNL.¹⁷) This process consists of extruding a Nb-Cu composite and drawing it to a final size; e.g., 300 μ m. Then, the wire was coated with a

a layer of tin before heating it to make a Cu-Sn alloy matrix and then Nb_3Sn 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_3Sn filaments. The primary difficulty is delamination of the outer layer of the wire¹⁸ when the plated Sn layer was greater than $\sim 5 \mu\text{m}$.¹⁹ Thus, the maximum wire size for this process was limited to $\sim 0.25 \text{ mm}$ in diameter because a thicker Sn layer is required for complete reaction of Nb to Nb_3Sn 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.²⁰ 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.²¹ This consists of an annealing step at ~ 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 $\sim 13 \text{ wt\%}$ as in the case of the "bronze process".

A high Sn concentration in the matrix normally results in a high critical-current density for Nb_3Sn 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 ($\sim 30 \mu\text{m}$). 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.^{22,23} This process consists of assembling Cu-clad Nb-bars and a Cu-clad (Sn-20 at.% Cu) alloy* rod

*It was shown later that a pure Sn rod can also be used for this purpose.²³

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_3Sn (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.^{24,25} Both of these employ Nb tubing instead of rods. In one case,²⁴ 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_3Sn (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_3Sn 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.²⁶ 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 ($7.6 \times 7.6 \text{ mm}^2$)²⁶ and a large enough quantity of wire to make test coils²⁷ 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 (Nb, Nb₃Sn) and the matrix. Although the ratio of the bronze-to-the core (Nb+Nb₃Sn) is quite small (less than 1) producing a small longitudinal compressive strain on the Nb₃Sn layer, it turns out that a large radial tensile strain exists due to the contraction of the bronze at the core area.^{28,29} This strain reduces T_c ^{26,28,30} and J_c ²⁶ 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 Nb₃Sn filaments.²⁸ 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_3Sn 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_3Sn 's mechanical property (the "strain tolerances" of the conductor³²) 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 ($\sim 30 \mu\text{m}$) 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 Al5 filamentary conductors was proposed by C. C. Tsuei in 1973.^{33,34} 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_3Sn . 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_3Sn or V_3Ga wires due to the close proximity of finely divided ($< 1000 \text{ \AA}$) 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 temperature³⁵ while the other extrudes it at an elevated temperature ($\sim 1000^\circ\text{C}$ 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 Nb_3Sn 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 Al5 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 Nb-Sn diffusion couple and then compare the formation of phases in a Nb-(Cu-Sn), a Nb-(Cu-Ge), and a V-(Cu-Si) couple.

Commercial Nb_3Sn tapes have been produced for many years by heating Nb or (Nb-1% Zr) tapes in a liquid tin bath. When these tapes are heated at temperatures above $\sim 930^\circ\text{C}$, single-phase Nb_3Sn 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, Nb₆Sn₅ 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 terminating phase is determined by the relative thermodynamic stability. As a means to calculate the relative stability, the stability index, S.I. was introduced by Raynor⁴⁰ and is a convenient measure of the relative thermodynamic stability of phases. The stability index for a compound A_xB_(1-x) is defined as

$$S.I. = T_m [T_B + (T_A - T_B)(1 - x_B)]^{-1} \quad (1)$$

where T_m , T_A , and T_B are the melting temperatures for the compound, the elements A and B, respectively, and x_B is the atomic fraction of B in the compound. 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 stability 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 Al5 compound layer, multiphase nonsuperconducting compound layers, and an Al5 phase and a nonsuperconducting phase layers are formed in these systems, respectively.

The first case (Nb-Cu-Sn) is an example in which the Al5 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,⁴³ Dew-Hughes⁴⁴ constructed a part of a section of the Nb-Cu-Sn ternary phase diagrams at $\sim 700^\circ\text{C}$, and this is shown in Fig. 6. This diagram shows that the diffusion path from the Cu-Sn solid solution to the Nb-Sn solid solution passes through only the Al5 Nb_3Sn 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 Al5 phase field in this diagram does not reflect some of the experimental observations: 1) T_c of Nb_3Sn is always ~ 18 K regardless of the composition of the bronze, indicating the composition of Nb_3Sn at the bronze interface is nearly 25 at.% Sn, and 2) the amount of Cu in Nb_3Sn varies with the Sn concentration in the matrix.⁴⁵ 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 V_3Ga layers are not available from the literature. Thus, the Al5 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 Al5 phase for Nb_3Sn and V_3Ga are significantly different. The maximum amount of Sn in Nb_3Sn is ~ 25 at.% while that of Ga in V_3Ga is ~ 30 at.%. The difference in the reaction temperature dependence of T_c between Nb_3Sn and V_3Ga (see Section III) may originate in this phase-field difference. However, without detailed diagrams of this region of the V_3Ga 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 Al5 phase. There is no direct tie line to the Al5 phase, and more importantly, as pointed out by D. Dew-Hughes⁴⁴ the Al5 may not even lie on the direct tie-line route from the most stable phase to the Nb-solid solution as shown in Fig. 7.⁴⁴ In fact, there appears to be two stable phases based on Nb_5Ge_3 and Nb_3Ge_2 . Thus, the superconducting Al5 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.^{44,46} In this system two diffusion paths are possible as indicated. One from a low Si bronze (Si < 1 at.%) goes directly to V_3Si ; and the other, from the bronze with higher Si content, goes to V_3Si via V_5Si_3 . Thus, Al5 V_3Si can be formed from a low-Si bronze or from a high-Si bronze with a V_5Si_3 layer.^{46,48} 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 Al5 phase and the solid solution (Cu-Ge) as in the case of the V-Cu-Si system.⁴⁹

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 $\text{Nb}(\text{Al}_x\text{Cu}_{1-x})$ block the tie line between the Cu-Al

bronze to the Al₅ phase.⁵⁰ Thus, the superconducting Nb₃Al 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 Al₅ compounds can only be produced by the "bronze 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 quaternary 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 Al₅ 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,^{51,52} and the treatment of the layer growth via a grain-boundary diffusion mechanism by H. H. Farrell et al.^{53,54} 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.⁵¹ For simplicity only the system Nb-Cu-Sn is discussed here, but the formation of V₃Ga 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 Al₅-phase field, we can make a schematic pseudobinary phase diagram as shown in Fig. 10 and the diffusion path at ~700°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 Nb_3Sn will form at the left interface with a growth rate $dX/dt = J_{Sn} V_f$ where X is the thickness of the compound Nb_3Sn , t is time, V_f is the volume of Nb_3Sn 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- Nb_3Sn 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:

$$J_{Sn} = D \left. \frac{dc}{dx} \right|_{Nb-Nb_3Sn} \approx D \frac{\Delta C}{X} \quad (2)$$

where D is the diffusion constant of Sn in a Nb_3Sn layer, and ΔC is the difference in composition across the layer at temperature T . As pointed out by D. S. Kopecki,⁵² the exact equation for J_{Sn} with moving interfaces is almost intractable. However, the form

$$J_{Sn} = (\alpha D \Delta C) / X \quad (3)$$

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

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

$$X^2 = 2\alpha D \Delta C V_f t \quad (4)$$

or

$$X = \sqrt{K_c t}$$

and this indicates that the growth in the couple is parabolic since $(2\alpha D \Delta C V_f)$ 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 μ across the layer. Then the flux at the Nb-Nb₃Sn interface is

$$J_{\text{Sn}} = \alpha M \Delta \mu / X \quad (5)$$

where M is the mobility of Sn through Nb₃Sn. When using this equation, we visualize a couple as shown in Fig. 11b. The point to remember here is that μ is continuous across the interfaces when equilibrium occurs at the interfaces. From Eq. (1) and Eq. (5), we again obtain a parabolic growth rate,

$$dX^2/dt = 2\alpha M \Delta \mu V_f = K \quad (6)$$

Thus, the growth rate of Nb₃Sn 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 Nb₃Sn-(Cu-Sn) interface will not be less than J_{Sn} at the Nb-Nb₃Sn 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 slower⁵⁶ 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 evidence⁵⁸ suggests that

the mechanism of growth is diffusion of Sn through Nb_3Sn grain boundaries as originally proposed by Farrell, Gilmar, and Suenaga⁵³ 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.^{59,60} In Whipple's formulation,⁵⁹ 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

$$D\nabla^2 C = \partial C / \partial t \quad (7)$$

in the bulk of the medium, and

$$D' \frac{\partial^2 C}{\partial x^2} + \frac{D}{a} \frac{\partial C}{\partial t} \quad \text{at } x=0 \quad (8)$$

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. Calculations⁵⁹ 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.⁵³ 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-Nb₃Sn 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 Nb₃Sn.

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.⁵³ 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_ϕ at a rate obtained from the conservation equation

$$\gamma \bar{L}^2 C_1 \frac{dX_\phi}{dt} = a \bar{L} D' \frac{C_o}{X_\phi}, \quad (9)$$

where $a \bar{L} / \gamma \bar{L}^2$ is the fraction of the area of the interface occupied by the grain boundaries, and γ is a geometrical factor depending on the shape of the grains. C_1 is the concentration of Sn at the growth front and C_o 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

$$X_{\phi}^2 = \frac{2C_o aD'}{C_1 \gamma} \int_0^t \left(\frac{\bar{L}}{\bar{L}^2} \right) dt \quad (10)$$

or

$$X_{\phi} = \left(\frac{2C_o aD'}{(1-m)C_1 \gamma \lambda_o(T)} \right)^{0.5} t^{0.5(1-m)} \quad (11)$$

where it was assumed that $\bar{L}^2/\bar{L} = \lambda_o(T)t^m$ 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_{ϕ} , 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 rate for Nb_3Sn 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_3Sn 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_3Sn ⁵⁵ and V_3Ga 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, μ , in the matrix requires lowering it in the compound at the interface since μ has to be continuous at the interface. Such reduction may imply that the Sn concentration in Nb_3Sn 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 μ 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 ($\sim 10^2$) larger than that in the Nb_3Sn layer, such a gradient is not expected to exist. Furthermore, experimental results⁶² 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_3Sn and thus the growth rate for the layer without changing the bulk concentration of Sn at the Nb_3Sn -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 $\text{Sn} \approx 18$ at.% and ~ 26 at.%. This is in agreement with early compositional profile measurements⁶⁴ and a more recent study⁶⁵ (Fig. 13) indicating essentially no change in the composition along the Nb_3Sn 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.⁵³ 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 Al5 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_3Sn , 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.^{55,66-70} However, when "flattened" wires were used for the study, the layer growth was characterized by the $t^{1/2}$ law very well.^{58,71,72} The difference in this growth

behavior in the bronze-processed Nb_3Sn 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 Nb_3Sn layers. Since Sn migrates to the Nb- Nb_3Sn interface much faster than Nb moving out to the Nb_3Sn -bronze interface, there will be large internal pressures due to formation of Nb_3Sn built up near the Nb- Nb_3Sn interface pushing out the existing Nb_3Sn 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 Nb_3Sn at the Nb- Nb_3Sn interface leading the layer growth $\sim t$. 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 Nb_3Sn -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 Nb_3Sn) 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- Nb_3Sn interface at the same rate as the Sn atoms move into the Nb_3Sn , 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 A15. A composition profile of a $\text{Nb}_3(\text{SnGa})$ 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 Nb_3Sn -Nb interface as shown in Fig. 14.⁷³ 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- Nb_3Sn 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 character 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 expected 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.⁵⁵ 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 $\sim t^{0.5}$. 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,⁷⁴ 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_3Ga , the geometry of the core is not as critical as in the case of Nb_3Sn . From the absence of the Kirkendal voids in multifilamentary V_3Ga 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_3Ga interface, and thus no cracks will be formed. In most cases, the time dependence of layer growth was observed to be parabolic.^{11,57,75} However, when the V cores are alloyed with Zr or Ti (greater than 1~2 at.%), extensive Kirkendal voids appear at the V_3Ga -(Cu-Ga) interface suggesting an increased Ga-diffusion rate relative to that for V.^{76,77} 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_3Sn .^{76,77}

As stated earlier, another factor which influences the kinetics of the compound growth is the concentration of Sn or Ga in the matrix.^{11,55,78} In the

case of Nb_3Sn , the dependence of the growth rate of the Nb_3Sn layer on the Sn concentration in the matrix is nearly parabolic as shown in Fig. 15a.⁵⁵ Since the wires which were used for this study were circular and significant cracks were observed in the layers for Nb_3Sn 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.⁷¹ 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_3Ga where the cracks did not form. This is shown in Fig. 15b.¹¹ It is very interesting to note that according to these data, V_3Ga will not form in a reasonable range of time and temperature if the concentration in the matrix is reduced below ~ 13 at.%, while Nb_3Sn 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_3Ga was formed. This difference is probably a reflection of differences in detailed shapes of the Al5 phase fields for Nb_3Sn and V_3Ga 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_3Ga 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 Al5 layer. When the compound growth occurs at relatively high temperatures ($\sim 800^\circ\text{C}$ for Nb_3Sn and $\sim 700^\circ\text{C}$ for V_3Ga) 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_3Sn layer are shown in Figs. 16⁷⁹ and 17⁵⁸ 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_3Sn 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 Al₅ 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_3Sn 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 $\sim t^{1/2}$ 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_3Sn and V_3Ga 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.⁹ 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 Nb_3Sn 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 Nb_3Sn primarily to vary the intrinsic superconducting properties, T_c and H_{c2} , of the compound.

Zr^{56} and Hf^{80} are the first type. Because (Nb-1 at.% Zr) substrates were used in the liquid diffusion process for fabrication commercial Nb_3Sn tapes, Zr was first tried to study its influence on the critical-current density of the bronze-processed Nb_3Sn wires.⁵⁶ In this study, a 0.5 wt% addition to Nb cores enhanced the growth of Nb_3Sn layers by approximately a factor of two from the unalloyed Nb. But a 2.5 wt% addition dropped the growth by ~50% from Nb_3Sn 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 Nb_3Sn grains was slowed compared with the Nb_3Sn 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 Nb_3Sn layers and some depletion of Sn in the matrix, thus resulting in $\sim t^{0.35}$ 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 Nb_3Sn grains to increase the growth of the compound as with the Zr addition.

The addition of Ta to the core increased the growth.^{70,81} However, the reason for this increase is not clear. The grain sizes appeared to be approximately equal for pure Nb_3Sn and $(\text{NbTa})_3\text{Sn}$ or to be somewhat larger for the Ta-containing Nb_3Sn . 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_3Sn 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,⁸² Al,^{67,68} Au,⁸² Ga,^{80,83} Ge,^{82,84,85} In,⁶⁸ Mg,⁷⁷ Sn,⁶⁶ and Zn⁷¹ have been added to the bronze (Cu-Sn) matrix to investigate the effects of these additions on the superconducting properties of Nb_3Sn . Among these only Ga was incorporated in Nb_3Sn 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,⁹ it is reported that Sn's chemical activity is substantially increased by the addition of Zn in a Cu-Sn alloy.^{86,87} 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_3Sn and Nb_3Ge_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. 19.⁵⁸ The increased growth with the Mg addition is most significant at high temperatures, but the growth is essentially unaltered at $\sim 700^\circ\text{C}$ which is the temperature of most heat treatments for Nb_3Sn .

multifilamentary wires. In this study Togano et al.⁵⁸ have clearly identified that the refined grain size in the Nb_3Sn 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_3Sn 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_3Sn 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_3Sn 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.^{53,54} is an appropriate one for describing the growth of Nb_3Sn 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 V_3Ga , only 3 elemental additions, Al^{89,90} and Mg⁹¹ to the bronze and Ga^{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 V_3Ga 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.⁹⁰ 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 (~ 3 at.%⁹⁰) 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 Mg⁹¹ in the matrix and additions of Ga^{84,85} 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 .⁹¹ 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, ΔG , 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 (5.4×10^{-19} J) but was reduced (4.9×10^{-19} J) when Mg was added.⁹¹ 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_3Ga with the (V-6 at.% Ga) core and the matrix without Mg is higher than that for (b) V_3Ga 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_3Ga composites.

Although it was reported⁹¹ that the additions of Ga and Mg increased the Ga content in V_3Ga from 22.5 to 23.5 at.% for V_3Ga without and with the additions, respectively, there was not enough T_c change (~ 0.3 K) to be consistent with such a large increase in the Ga content. According to Das et al.,⁹⁴ a change of ~ 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.⁷⁷ The addition of Ti probably also makes the dependence nonparabolic but sufficient data are not available at this time.⁹⁵

There are other Al₅ compounds which can be formed by the bronze process such as V₃Si,^{46,96,97} V₃Ge,⁹⁸ 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 Nb_3Sn and V_3Si (which are stable to over 2100°C). Thus, thermodynamic driving forces for nucleation of new grains are higher for Nb_3Sn and V_3Si and the diffusivity of Ga and V higher for V_3Ga . Both may contribute to the larger grains found in V_3Ga .

In contrast to the above observation, Farrell et al.⁵³ found a columnar growth in a 19-core Nb_3Sn which was formed at 800°C. Pande⁷⁹ 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 Nb_3Sn multifilamentary wires⁹⁸ as well as monofilamentary Nb_3Sn ⁵⁸ and V_3Ga ^{91,99} 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.¹⁰⁰ found for multifilamentary Nb_3Sn 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 Nb_3Sn 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 Nb_3Sn and V_3Ga tapes were measured and reported by Togano et al.¹⁰¹ The Nb_3Sn layers and the substrates, V and Nb, of the bronze-processed V_3Ga and Nb_3Sn exhibited very strong (100) <011> texture. In the surface-diffusion processed V_3Ga , 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 Al5 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 Al5 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 Al5 compounds fabricated by the bronze process as a function of the matrix-to-core ratio.¹⁰² Here the difference in T_c is defined as $[\Delta T_c = T_c \text{ (with the matrix)} - T_c \text{ (without the matrix)}]$. As shown in the figure, the presence of the matrix can increase or decrease T_c as much as ~ 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.²⁸) As mentioned earlier, when a composite wire consisting of Nb, Nb₃Sn, and a Cu-Sn alloy matrix (Nb₃Sn is used for an example for convenience for this section) is heated at elevated temperatures (~700°C) and cooled to low temperatures (~4 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 α for Nb and Nb₃Sn are essentially identical, we only consider the difference between those for the core (Nb and Nb₃Sn) and the matrix. Then, based on force and length balance, the longitudinal strain ϵ_c in the core is given by

$$\epsilon_c = -\Delta\alpha\Delta T (E_m/E_c)(R^{-1} + E_m/E_c)^{-1} \quad (12)$$

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.²⁸) Also, neglected here are the effects of plastic strain of the matrix as well as the Nb core at moderate temperatures during the cool-down process.^{28,103}

Following the phenomenological development by Testardi¹⁰⁴ and Welch,²⁸ we simply assume that the critical-temperature dependence on strain is

$$\Delta T_c = -A \epsilon_c^2 \quad (13)$$

where A is a proportionality constant. If $E_m \approx E_c$ is assumed. (This assumption may not be correct at low temperatures as shown by Bussiere et al.¹⁰⁵ that the modulus for Nb₃Sn is decreased by a factor of 2 as temperature is lowered to $\sim T_c$ 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, ΔT_c only depends on $(\Delta \alpha \Delta T)^2$. The observed ΔT_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. 24¹⁰⁶ and 25.¹⁰⁶ 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 Nb₃Sn.¹⁰⁷ The variation in H_{c2} with strain is shown as H_{c2}/T_c vs R. An analysis⁽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 Nb₃Sn was alloyed with Ga by an addition of Ga to the Cu-Sn matrix, ΔT_c for Nb₃(SnGa) was significantly reduced¹⁰⁸ while the addition of Ta to the compound increased ΔT_c from 1.0 K for pure Nb₃Sn to 2.2 K for Nb₃Sn from a Nb-10 wt% Ta core when the wires were heat treated for 16 h at 725°C.¹⁰⁹

Earlier, it was shown that ΔT_c for a given wire decreased with increasing annealing time at 725°C ³⁰ indicating that the disorder in A15 structure also increased the sensitivity of Nb_3Sn to the strain. This observation was further clarified by studying ΔT_c as a function of neutron irradiation,¹¹⁰ and the result is shown in Fig. 26. The physical mechanism for these observed strain sensitivities in Nb_3Sn 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 Nb_3Sn 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 A15 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 Nb_3Sn and V_3Ga which are produced by the bronze process depend on a number of parameters, reaction time and temperatures, compositions of the matrix, 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 of these compounds. In this section, an attempt is made to distinguish various variables and to measure their influence on T_c for Nb_3Sn and V_3Ga . Metallurgical effects on T_c for V_3Si , V_3Ge , and V_3GeAl 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 $\sim 150 \mu\text{m}$) and a fine multifilamentary commercial wire (filament $\sim 3 \mu\text{m}$), respectively.³⁰ It is interesting to note that in both cases, T_c of Nb_3Sn reaches 17.9 K after 6 h at 725°C when all prestrains due to the matrix are removed. This indicates that Nb_3Sn 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 ($\ll 1 \mu\text{m}$) tend to have lower T_c . This, according to Auger chemical analysis and profiling of Nb_3Sn layers, is due to a deficiency of Sn in the layer.⁶⁵] 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_3Sn can establish faster when the filaments are fine. This is probably due to completion of reaction for formation of Nb_3Sn 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_3Sn layer before a section of well-ordered Nb_3Sn is made during the growth if the entire Nb is not consumed for Nb_3Sn . It is also interesting to note that T_c with the matrix-on can give an indication of a relative order in Nb_3Sn . In other words, the depression in T_c due to the matrix is larger if the ordering in Nb_3Sn 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 Nb_3Sn 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 Nb_3Sn . 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 Nb_3Sn .

T_c of Nb_3Sn 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 Nb_3Sn which are given for a constant thickness of Nb_3Sn 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 Aihara¹¹¹ does not meet this criterion completely but this is the best study available in investigating T_c of Nb_3Sn 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_3Sn which was obtained for this temperature than all the others. But others^{65,66} 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.⁶⁵ Also shown are the corresponding lattice parameters a_0 for each Nb_3Sn 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_3Sn due to the site exchanges between Nb and Sn is less likely since high- T_c Nb_3Sn 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_3Ga (see below), but unfortunately, there is not any experiment systematically studying such effects on the T_c of Nb_3Sn . However, observing T_c for Nb_3Sn wires which are made from a Cu-13 wt% Sn and Cu-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_3Ga , 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. 30.⁹⁹ For V_3Ga 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_3Ga 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_3Ga 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.,⁷⁷ 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,¹³ and Howe et al.¹¹² 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 $600^\circ C$ in contrast to the results by Tanaka et al.⁹⁹ 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.,⁹⁴ 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_3Sn 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_3Sn ⁸⁰ while essentially all of Ta in the core is incorporated in the layer.⁷⁰ Sekine and Tachikawa⁸⁰ reported that the additions of both Zr and Hf increased T_c of the compound up to ~ 0.5 over T_c for pure Nb_3Sn 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 ~ 0.2 K, and with Zr additions significantly thicker layers are required to achieve a saturation of T_c .⁵⁶ For example, 17.8 K for T_c of the pure Nb_3Sn was reached at ~ 1.5 μm thick layer while T_c of 17.6 K for Nb_3Sn with 0.5 or 2.5% Zr in the core was obtained at a ~ 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_3Sn with 0.5% Zr in the core only reached ~ 17.2 K at ~ 7 μm layer thickness when it was formed at 650°C . Perhaps, these results indicate that the crystallographic order in Nb_3Sn 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_3Sn 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. (Nb_3Sn ~ 18 μm , and Nb_3Sn with 2 at.% ^{Zr} 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 Nb_3Sn is smaller, and T_c reduction due to the matrix is less. Therefore, the observed increases in T_c 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 T_c of Nb_3Sn .

The effect of Ta addition to Nb_3Sn through core alloying was carefully studied, and the result is shown in Fig. 33.¹⁰⁹ It is interesting to note that a small addition (~ 1.5 at.%) of Ta increased T_c of Nb_3Sn by ~ 0.3 K, but this increase in T_c was only revealed after the matrix was removed since T_c with the matrix intact monotonically decreased with the Ta concentration in the core. Also, the differences in T_c with heat treatment time at 725°C are very much greater with the matrix than without as mentioned for the pure Nb_3Sn ; i.e., the reduction in T_c is greater in the disordered Nb_3Sn than in the ordered Nb_3Sn . This example again clearly points out the importance of the prestrain from the matrix in determining T_c of the wires and in understanding variations in T_c with heat treatment and alloying. Another interesting aspect of this study is that the strain sensitivity of Nb_3Sn as measured by T_c for the wires with and without the matrix increased with small Ta additions but at high alloying contents of Ta in Nb_3Sn it decreases approximately to the value for the unalloyed Nb_3Sn .¹⁰⁹ 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 Nb_3Sn 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 ~ 0.3 K over the value for the pure Nb_3Sn . 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_3Sn layer and no influence on T_c due to the addition was noted.⁵⁸ However, all other additions tends to slow down the time to reach the maximum T_c (~ 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 Si¹¹⁵ 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_3Sn 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 strains²⁸ can strongly influence the critical-current density. The correlation of changes in J_c with such metallurgical variations in the Nb_3Sn 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 law¹¹⁶ for magnetic flux pinning is described, and its applicability to the bronze-processed Nb_3Sn 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 studies¹¹⁶⁻¹¹⁹ of type-II superconductors have indicated that the variation of the bulk pinning force density, $F_p = |\vec{J}_c \times \vec{H}|$, with magnetic field and temperature can be described by an equation

$$F_p = AB_{c2}^m(T)f(h) \quad (15)$$

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 $f(h) = h^l(1-h)^n$ and l and n may change from one superconductor to another. In the investigation of Nb_3Sn wires, the scaling law developed by Kramer¹¹⁶ 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 model¹¹⁶ 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

$$F_p = |\vec{J}_c(H) \times \vec{H}| = K_s h^{1/2}(1-h)^2 \quad (16)$$

and

$$F_p = |\vec{J}_c(h) \times \vec{H}| = K_p h^{1/2} (1-h)^{-2} \quad (17)$$

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

where

$$h = H/H_{c2}, K_s = 0.56 H_{c2}^{5/2} K_1^{-2} (1-a_0 \sqrt{\rho})^{-2},$$

$K_p = 5 \times 10^6 \rho P \omega^4 \beta^4 H_{c2}^{5/2} (\phi_0^{1/2} K_1^2)^{-1}$, and κ_1 is the Ginsburg-Landau constant ($\kappa_1 = H_{c2}/\sqrt{2} H_c$), a_0 is the flux lattice spacing [$a_0 = (\phi_0/H)^{1/2}$] and ρ is the density of flux-pinning sites, β is a constant, ω 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_{pmax}) 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.¹²² Simple algebraic manipulation of Eq. (16) yields:

$$J_c^{1/2} H^{1/4} (1-a_0 \sqrt{\rho}) = 0.7 \kappa_1^{-1} (H_{c2} - H) \quad (18)$$

Now, since the right-hand side of Eq. (18) is linear in H , the equation can

be used to determine H_{c2} by plotting the left-hand side against H and extrapolating

In most cases, at sufficiently high field, $a_0\sqrt{\rho} \ll 1$, $J_c^{1/2}H^{1/4}$ 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 κ_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 Nb_3Sn wires with regard to: 1) the linear dependence of $J_c^{1/2}H^{1/4}$ on H , and 2) the values of κ_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 ~ 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 $a_0\sqrt{\rho} \ll 1$ 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 (~ 8 to ~ 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 superconductivity 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 (~ 2 T) than the H_{c2} as determined by linear extrapolation. This is probably due to inhomogeneities in the Nb_3Sn such as a composition variation across the Nb_3Sn layer or a variation in the strains due to the matrix.²⁸ It is also possible that the bulk of the Nb_3Sn 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. (18) 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_3Sn wires show that J_c varies with magnetic field as described by Eq. (18) with $a_0\sqrt{\rho} \ll 1$, 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 $a_0\sqrt{\rho} \ll 1$. This behavior is illustrated in Fig. 35 which show data for an "in-situ processed" wire, heat treated at 550°C for 6 days.¹²³ A similar result was also obtained for a "bronze processed" Nb_3Sn wire which was electron irradiated during a 500°C heat treatment.¹²⁴ As shown in the figure, the data can be made to produce a wide region of linearity in the plot if the $(1-a_0\sqrt{\rho})$ 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_3Sn is $\sim 400 \text{ Å}$ ¹²³ 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_3Sn . 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-Ga¹²⁵). 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 Tachikawa⁸⁰ are also included. It is speculated that the deviation from linearity for these wires is due to the paramagnetic limit on H_{c2} ,¹²⁵ 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.⁹⁹ reported the observation of very large differences in J_c of bronze-processed V_3Ga tapes which are measured with applied fields parallel ($J_{c||}$) and perpendicular ($J_{c\perp}$) 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 .¹²² 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_{c1} is larger than J_{c2} , but only by 30 to 40%. These smaller differences in J_c are probably due to nearly equiaxed growth of Nb_3Sn 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 κ_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_{c1} and J_{c2} is essentially the same in both cases. Unfortunately, the values of H_{c2} for these tapes are significantly lower than those for Nb_3Sn 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_{c1} and J_{c2} 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 κ_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 ~ 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 κ_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 κ_1 so obtained are smaller than that expected for Nb_3Sn , for which the smallest expected value is ~ 20 for very clean specimens.¹²⁶ 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 κ_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 κ_1 :^{28,126,127}

$$\frac{H_{c2}}{T_c} = c[N(0)(1+\lambda)]^{1/2}(1-t^2)\kappa_1 = c'\gamma^{1/2}(1-t^2)\kappa_1 \quad (19)$$

where c and c' are numerical constants, $N(0)$ is the density of states at the Fermi level, λ is the electron-phonon coupling constant, γ is the electronic specific heat coefficient and $t = T/T_c$. Recent experimental studies¹²⁶⁻¹³⁰ of the effect of disorder and nonstoichiometry on the superconducting properties of a variety of Al₅ compounds show $N(0)$, λ , and γ 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 $N(0)$, λ , 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 κ_1 to remain more-or-less constant, yet, as seen from Table 1, the value of κ_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_3Sn , the interpretation of parameters such as " κ_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 κ_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 κ_1 as determined from Eq. (18) is qualitatively correct with regard to changes in κ_1 with alloying and irradiation by high energy neutrons of Nb_3Sn wires. For example, when Nb_3Sn 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.⁷⁰ (See Fig. 40.) Also, a similar change in κ_1 or $[\Delta(J_c^{1/2} H^{1/4})/\Delta H]$ was observed with increasing neutron fluence when Nb_3Sn wires were irradiated with neutrons ($E > 1$ MeV) at ambient temperature.¹³¹ In both of these cases, it is expected that the normal resistivity increased with alloying or irradiation, thus increasing the value of κ_1 or decreasing the slope in $J_c^{1/2} H^{1/4}$ versus H plots. Therefore, in these cases, the trend in κ_1 determined by Eq. (18) is as one expects in Nb_3Sn .

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, $J_c H$ for a bronze-processed Nb_3Sn 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.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 $J_c H$ 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, $J_c H$ is proportional to $H_{c2}^{5/2}(T)$ in both high- and low-field regions.

The first measurements of $J_c(T)$ for Nb_3Sn and V_3Ga multifilamentary wires were made by Crow and Suenaga¹³² and the results are shown in Figs. 41 and 42, respectively. More recently, similar measurements were performed on fine multifilamentary wires¹³³⁻¹³⁵ 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_3Sn than in V_3Ga . 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,¹³⁶ 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

$$R' = \omega_0 \exp(-F_b/kT) \quad (20)$$

where ω_0 is a vibrational frequency of the flux bundle and

$$F_b = F_p - JH\lambda^2\xi_0 \quad (21)$$

where F_p is the pinning energy, l is the length of the flux line which the force is acting on, and λ and ξ_0 are the penetration depth and the coherence distance, respectively. At a measurable critical rate R'_c ,

$$kT \ln (R'_c / \omega_0) = -(F_p)_{\text{critical}} \quad (22)$$

or

$$J_c = [F_p - kT \ln(R'_c / \omega_0)] (H l \lambda^2 \xi_0)^{-1} \quad (22a)$$

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 Nb_3Sn than in V_3Ga . Thus, this deviation is significantly larger in Nb_3Sn 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 Nb_3Sn monofilamentary wires were critically examined by Schauer and Zimmermann¹³⁵ and Kroeger et al.¹⁰⁷ 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 Nb_3Sn 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 result¹³⁷ on the measurements of the pinning force for a bronze-processed Nb_3Sn wire with a matrix-to-core ratio of ~ 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.¹³⁸ that J_c in the bronze-processed Nb_3Sn 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_3Sn and V_3Ga and these are summarized in the following.

Comparison of the earlier results on Nb_3Sn ¹³⁸ and V_3Ga ⁹⁹ indicated that the critical-current density for Nb_3Sn was smaller by an order of magnitude than for V_3Ga at a given grain size.⁹⁷ However, Livingston showed that the dependence of J_c on the grain size is essentially identical for Nb_3Sn , V_3Ga , and V_3Si if these are produced in an identical manner⁹⁷ 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_3Sn and V_3Si 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.¹⁰⁶ 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. 43⁹⁷ 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 calculation¹³⁹ 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 ($\sim 500-700 \text{ \AA}$) 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 $D \sim 1200 \text{ \AA}$. 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 became small, are from the wires heated at very low temperatures ($\sim 600^\circ\text{C}$), 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_{c2} and H_{c2} 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 Nb_3Sn 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_3Sn and V_3Ga 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_3Sn 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_3Sn ($>2\sim3\mu m$), 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_3Sn compound layers thicker than ($2\sim3\mu m$), 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,^{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_3Sn 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 factor⁵⁶ for the growth of the layer. Also, in Fig. 19, the dependence of J_c at 6.5 T on the reaction temperature is shown⁵⁸ and such a drastic decrease in J_c of Nb_3Sn with the temperature is a reflection of the larger Nb_3Sn grains at the high reaction temperatures as shown in Fig. 22.

Similar decreases in J_c of V_3Ga due to high reaction temperatures were also observed.^{13,61} At the very high-magnetic fields, ($H \gg 12$ 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 Nb_3Sn 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 ρ_N , b) the critical temperature and c) grain sizes. ρ_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 ρ_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 Nb_3Sn , 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 Nb_3Sn 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 addition⁷⁰ 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 ρ_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_3Sn from the value of J_c for the unalloyed Nb_3Sn 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_3Sn 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_3Sn and $(Nb-Ta)_3Sn$ 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_3Sn . 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_3Sn with Hf additions slightly increased with the Hf content in the core.⁸⁰ 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 ρ_N . These additions were also found to limit the grain growth in Nb_3Sn . The first indication of reduced grain growth with Zr addition was shown by Suenaga et al.⁵⁶ When J_c versus thickness was plotted for the early Nb_3Sn wires, the rate of the decrease in J_c with increasing thickness was slower with Zr in the core than in pure Nb_3Sn . 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^{144} and Hf^{80} (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 Nb_3Sn as shown by Togano et al.⁵⁸ (Figs. 17 and 19). 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 ~ 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 Nb_3Sn layer growth rate and increased J_c at 4 T, probably due to refinement of the grains.⁶⁶

Both additions of Al ⁶⁷ and Zn ⁷⁵ to the matrix in some cases increased the layer growth rate, but J_c 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 J_c 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 T_c and H_{c2} of Nb_3Sn .^{80,83} (See Table ~~1~~¹ for example.) In this case, Ga is incorporated in the A15 structure, probably at Sn sites. However, the growth rate of the compound was considerably slowed by the addition and the grain size of $\text{Nb}_3(\text{SnGa})$ increased significantly over that for pure Nb_3Sn , thus resulting in a reduction of J_c from the value of J_c for the unalloyed wires except at very high magnetic fields (Fig. 4~~1~~⁶). The use of alloyed Nb cores with Zr and Hf in conjunction with the matrix increased the growth rate^{80,83} and J_c for $H \gtrsim 10$ T increased by considerable amounts^{80,83} over the value for the wire with the Cu-Sn-Ga matrix. The observed increases in high field J_c appear to be due to increased H_{c2} by the incorporation of Ga and Zr or Hf in Nb_3Sn . (See Table 1.) An interesting aspect of the Ga addition to Nb_3Sn with respect to the magnetic field dependence of J_c is pointed out in the previous section that J_c does not follow a $h^{1/2} (1-h)^2$ dependence while essentially all other data of J_c for Nb_3Sn follow this dependence. (See Fig. 36.)

In spite of the observed significant increases in J_c at high fields and in J_c of Nb_3Sn 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_A and Ta 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 atm%) to the core appear to produce Nb₃Sn with J_c nearly as high as that for Ta alloyed wires.¹⁴⁴

In contrast to the study of Nb₃Sn, a relatively smaller number of elemental additions to V₃Ga 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 additions⁸⁹ 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 V₃Ga wires decreased with alloying beyond 2 at.% Al, probably due to decreased H_{c2} and T_c. The addition of Al to the V core⁹⁰ also resulted in comparable J_c for V₃Ga 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_3Sn , a small addition of Mg to the matrix dramatically increased the growth rate of V_3Ga (see Fig. 20) and increased J_c significantly.⁹³ 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 6 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_3Ga . 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_3Ga which was formed in a composite of a (V-9.5 at.% Ga) core and a (Cu-17.5 at.% Ga) matrix.¹⁴⁵ J_c at 15 T was $3 \times 10^5 \text{ A/cm}^2$ 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.¹⁴⁶

A small addition (0.5 at.%) of Mn is also known to increase the growth rate and the critical current density of V_3Ga due to refinement of the grains.¹¹⁴ 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 Nb_3Sn and V_3Ga wires and metallurgical treatments are summarized. First, we will restate important observations regarding the J_c of Nb_3Sn 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, $HJ_c \sim h^{1/2}(1-h)^2(1-a_0\sqrt{\rho})^2$ 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 ($H > 16$ 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:

$$J_c^{1/2}H^{1/4} = f(\sqrt{\rho}, \kappa_1) \frac{(H_{c2}-H)}{(1-a_0\sqrt{\rho})} \quad (23)$$

where f is a function of the pinning site density and κ_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

$$J_c H = \frac{A \rho^{1/2} (H_{c2} - H)^2 H^{1/2}}{\kappa_1^2 (1 - a_o \sqrt{\rho})^2} \quad (25)$$

where $A = A^{1/2}$. It is very instructive, as pointed out by D. O. Welch,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

$$\frac{\Delta J_c}{J_c} = \frac{1}{2} \left[\frac{1 + a_o \sqrt{\rho}}{1 - a_o \sqrt{\rho}} \right] \frac{\Delta \rho}{\rho} + \left(\frac{2H_{c2}}{H_{c2} - H} \right) \cdot \frac{\Delta H_c}{H_c} + \left(\frac{2H}{H_{c2} - H} \right) \frac{\Delta \kappa_1}{\kappa_1} + \frac{\Delta A}{A} \quad (26)$$

A particularly interesting aspect of Eq. (26) is that the change in J_c due only to κ_1 cannot produce the crossing behavior in the plot, $J_c^{1/2} H^{1/4}$ vs H , as shown in Fig. 40 with alloying Ta in the core. If the dependence of f on κ_1 is κ_1^n where $n > 1$, then, the equation will contain the crossing behavior with increasing κ_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 κ_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 $J_c^{1/2} H^{1/4}$ vs H plot is suspected to be due to the reduction of the pinning strength, ΔA 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 ($8 < H < 16$ 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_3Sn 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_3Ga 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 (~ 30 T). However, it is hoped that the above conclusions for Nb_3Sn can be qualitatively extended to the behavior of J_c in the V_3Ga 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_3Sn -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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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 2×10^3 A/cm².

Specimen	Heat treatment (°C x h)	T_c (K)	H_{c2} (4.2 K) (T)
A: Nb/7 Sn	800 x 100	17.1	17
B: 2 Zr/7 Sn	800 x 100	17.3	17.5
C: 2 Hf/7 Sn	800 x 100	17.5	19
D: 5 Hf/7 Sn	800 x 100	17.6	21
E: 2 Hf/5 Sn-4 Ga	800 x 100	17.7	~22
F: 5 Hf/5 Sn-4 Ga	800 x 20	17.7	~21.5
G: Nb/3 Sn-9 Ga	800 x 100	17.6	20
H: 5 Hf/3 Sn-9 Ga	800 x 20	18.0	~22.5

Table 2

Superconducting Properties of the Nb₃Sn Wires

	6h/725°C	16h/725°C	64h/725°C	96h/675°C
κ_1	9.2	9.9	13.8	8.66
$T_c^{(a)}$	16.15	16.45	16.85	16.80
$H_{c2}^{(b)}$	16.6	16.9	17.5	17.6

^aThe midpoint T_c measured inductively with the bronze matrix still present.

^bDetermined 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 Nb_3Sn and V_3Ga wires.
- Fig. 2. Schematic diagrams for formation of V_3Ga 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- Nb_3Sn -(Cu-Sn) diffusion couple. Dotted lines represent the concentration and the chemical potential in a grain boundary.

- Fig. 12. Schematic representation of a Nb_3Sn layer containing a grain boundary (Ref. 53).
- Fig. 13. Auger Sn depth profiles for Nb_3Sn layers which were heated at 650°C (Ref. 65).
- Fig. 14. A compositional profile of a $\text{Nb}_3(\text{SnGa})$ layer indicating an increased concentration of Ga at the Nb- $\text{Nb}_3(\text{SnGa})$ interface.
- Fig. 15. Concentration dependences of the a) Nb_3Sn and b) V_3Ga growth rates on a) Sn and b) Ga.
- Fig. 16. A transmission electron micrograph of Nb_3Sn grains growing at a Nb-(Cu-Sn) interface (Ref. 79).
- Fig. 17. Scanning electron micrographs of Nb_3Sn 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_3Sn 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_3Sn layer thickness and b) critical current densities at 6.5Ton heat-treating temperatures for Nb-(Cu-Sn) and Nb-(Cu-Sn-0.5 Mg) tapes (Ref. 58).
- Fig. 20. Dependence of V_3Ga layer growth rates on reaction temperatures for various composites (Refs. 89-92).
- Fig. 21. Critical temperature, magnetic fields, and currents of V_3Ga vs Al contents in the bronze (Ref. 91).
- Fig. 22. Grain size for bronze-processed Al5 compounds as a function of reaction temperature (Ref. 97).
- Fig. 23. Variations in T_c of Al5 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 $\sim 1 \mu\text{m}$ and $\sim 3 \mu\text{m}$.
- Fig. 32. Critical temperature of bronze-processed V_3Ga as a function of reaction temperature for ~ 1 and $\sim 2.5 \mu\text{m}$ thick V_3Ga layers.
- Fig. 33. Critical temperature of $(\text{Nb},\text{Ta})_3\text{Sn}$ 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 $J_c^{1/2} H^{1/4}$ 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 $J_c^{1/2} H^{1/4} (1 - a_0 \sqrt{\rho})$ vs H for an in situ Nb_3Sn wire which was heat treated at $550^\circ C$ for 6 days. This plot shows that the inclusion of $(1 - a_0 \sqrt{\rho})$ with $\sqrt{\rho} = (10^3 \text{ \AA})^{-1}$ 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_3Sn wires. These data do not appear to obey Eq. (18), (Ref. 122).
- Fig. 37. Critical current density of a bronze processed V_3Ga tapes vs magnetic field for applied field parallel ($J_{c\parallel}$) and perpendicular ($J_{c\perp}$) to the tape (Ref. 99).
- Fig. 38. Plots for $J_c^{1/2} H^{1/4}$ vs H for H parallel ($J_{c\parallel}$) and perpendicular ($J_{c\perp}$) to the surface of Nb_3Sn tapes (Ref. 122).
- Fig. 39. Plots for $J_c^{1/2} H^{1/4}$ vs H for a series of Nb_3Sn wires which were heat treated for 6, 16, and 64 h at $725^\circ C$ and for 96 h at $675^\circ C$ (Ref. 106).
- Fig. 40. Plots for $J_c^{1/2} H^{1/4}$ vs H for a series of Nb_3Sn wires which the cores were alloyed with Ta (Ref. 31).
- Fig. 41. Critical current density vs temperature at various magnetic fields for the Nb_3Sn multifilamentary wire.
- Fig. 42. Critical current density vs temperature at various magnetic fields for the V_3Ga multifilamentary wires.
- Fig. 43. Grain size dependence of critical-current densities of bronze-processed Nb_3Ga , V_3Ga , and V_3Si (Ref. 97).
- Fig. 44. Critical current density at 4 T vs reciprocal grain size for various bronze-processed Nb_3Sn wires (Ref. 140).
- Fig. 45. Critical magnetic fields for $(Nb,Ta)_3Sn$ wires as a function of the core composition (Nb-Ta), (Ref. 31).
- Fig. 46. Critical current density of Nb_3Sn tapes with Hf and Ga additions as a function of magnetic fields as indicated in Table 1 (Ref. 80).

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