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A15 MULTIFILAMENTARY SUPERCONDUCTORS BY THE INFILTRATION PROCESS*

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ABSTRACT

The inherent brittleness of the A15 compounds, and the requirement for a filamentary morphology, led to a heavy reliance on a powder approach for the preparation of superconducting tapes and wires. The quench-age technique, a non-powder process, was employed for the niobium aluminum system, following the special features of the equilibrium phase diagram. The powder approach proved particularly effective for binaries, such as Nb-Sn, and for the ternaries Nb(Al,Ge) and Nb(Al,Si). Two variations of the powder process were assessed. One involved the use of precompounded powder of the desired stoichiometry but required simultaneous application of heat and pressure. The second variation was the infiltration process. This process involves the preparation of a ductile niobium matrix containing a controlled network of interconnected pores which are subsequently infiltrated with liquid metals (Sn) or low melting-point eutectics (e.g., Al-Ge, Al-Si). The composite is then subjected to a thermomechanical treatment to form a multiply connected array of A15 filaments in a niobium matrix. Multifilamentary conductors, based on Nb₃Sn, Nb₃Al, Nb₃(Al,Ge) and Nb₃(Al,Si), were readily obtained. Nb₃Sn conductors made by the infiltration process exhibit a critical temperature (T_c) of 18.1 K and a critical current carrying capacity (I_c) of 8×10^4 amp·cm⁻² at 12 Tesla.

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REA

A15 MULTIFILAMENTARY SUPERCONDUCTORS BY THE INFILTRATION PROCESS

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INTRODUCTION

The morphology of practical superconductors is an essential consideration that is directly related to the requirement of conductor stability. An extensive treatment of stabilization criteria has been provided by the Rutherford Laboratory Superconducting Applications Group.¹ The adiabatic criterion is perhaps the most basic. For intrinsic stability, it requires that a superconductor should not exceed a critical size that is determined by certain properties of the superconducting material. In view of the adiabatic and the other criteria, the optimal size is generally considered to be less than 10 μm . From this requirement for such small sizes stems the preferred morphology for an intrinsically stable conductor: a large number of superconducting filaments arrayed in a normal matrix. Multifilamentary conductors were readily achieved with the ductile niobium-titanium superconducting alloy, and these have been developed to a high degree of sophistication, involving twisting, braiding and cabling. However, as shown in Table I, the superconducting properties of niobium-titanium do not compare favorably with those of the A15 compounds. Consequently a great deal of current research effort is devoted to the development of multifilamentary conductors based on the intrinsically brittle intermetallic compounds of the Nb_3Sn type.

The orthogonal chains of niobium atoms in close proximity are an important characteristic of the A15 structure. It is believed that the integrity of these chains strongly affect the

Table I. Some high field superconducting compounds
(niobium based)

COMPOUND	T_c ($^{\circ}\text{K}$)	H_{C_2} at 4.2 $^{\circ}\text{K}$ (Tesla)
$\text{Nb}_3(\text{Al}, \text{Ge})$	21	410
$\text{Nb}_3(\text{Al}, \text{Si})$	19.5	30
Nb_3Al	19	30
Nb_3Sn	18	23
NbTi	10	12

superconducting properties of the A15 compounds. Disruption of the chains by structural defects such as vacancies, or by tin atoms occupying niobium sites (in the case of Nb_3Sn), adversely affects the transition temperature (T_c) and the current carrying capacity. Thus in the design of processes for the fabrication of functional superconductors based on A15 compounds, two criteria have relevance in addition to the morphology constraints imposed by stability considerations. They are the stoichiometry and degree of order of the A15 phase. Most of the process development research presented in this report utilizes powder metallurgy techniques. There is one exception, involving the niobium-aluminum system, and it will be presented first.

THE NIOBIUM-ALUMINUM SYSTEM—A NON-POWDER APPROACH

This process^{2,3,4} takes advantage of the increasing solubility of aluminum in niobium with increasing temperature. At room temperature niobium can dissolve only 9 at. percent of aluminum, whereas at 1950 C the solubility of aluminum increases to 23 at. percent. It was reasoned that a sample heated into the high temperature solid solution region could be quenched rapidly enough to retain a metastable solid solution and prevent any transformation to the stable A15 phase. After quenching, the solid solution might be sufficiently ductile to permit plastic deformation. In that event, traditional processing techniques could be employed. Moreover, having the material in a metastable state would provide another important advantage: at an appropriate stage in the processing sequence, it could be transformed to the superconducting phase by a low temperature aging treatment. It is desirable that the A15 phase be formed at temperatures not exceeding 1000 C. The superconducting

properties of Nb_3Al are strongly dependent upon the degree of order of the niobium and aluminum atoms in the $A15$ lattice. For this reason, material formed by high temperature diffusion processes is often subjected to low temperature anneals of long duration. This restores much of the order which had been disrupted by the high temperature treatment. Furthermore, the critical current carrying capacity is related to the number and efficiency of the flux pinning centers present in the superconducting phase. Flux pinning centers can be oxides, vacancies or any other type of structural imperfection. Grain boundaries are very effective pinning centers; consequently, the smaller the grain size the better is the pinning effect. The grain size of the phase is directly related to its formation temperature. The lower the reaction temperature, the smaller is the grain size. A low reaction temperature is especially important for Nb_3Al , since no successful procedure has been developed to introduce a dispersed oxide phase, such as ZrO_2 , as pinning sites. For these reasons the quench-age approach appeared particularly attractive.

The process developed, which incorporates these ideas, is shown schematically in Fig. 1. Niobium tubing was used to sheathe a rod of grade 2011-T3 aluminum. This grade, which contains a small percentage of copper, provided a good match with the mechanical properties of niobium. The composite (O.D. = 5.8mm) was first swaged and then wire drawn to a diameter of 0.5mm. It was then heated for 30 seconds at a temperature of 1950 C to form a core of a saturated solid solution of aluminum in niobium. Direct resistive heating was used for two reasons: the time of the reaction could be regulated easily from seconds to minutes as desired, with the sample reaching the high temperature very rapidly; and the wire could be gripped in such a way that the ends were cooled. This eliminated any possibility of aluminum escaping from the ends. Quenching was accomplished by directing a jet of high pressure helium gas on the sample. The cooling rate achieved was approximately 550 C per second. Several observations confirmed the fact that at this stage the core was a metastable solid solution. Its microhardness value of 385 VH is similar to that obtained in a $Nb(Al)$ solid solution prepared by conventional techniques. No traces of the presence of the $A15$ phase were detectable by either metallographic or x-ray examination. However, following an aging treatment of one hour at temperatures from 850 to 1000 C, the microhardness of the core increased to 890 VH, a value characteristic of the $A15$ compound. The presence of the $A15$ phase after aging was further confirmed by x-ray analysis.

After quenching there are two options for further processing. The composite can be aged to transform the metastable solid solution core completely to the $A15$ phase. The second option, which is illustrated in Fig. 1, seems more interesting. Contrary

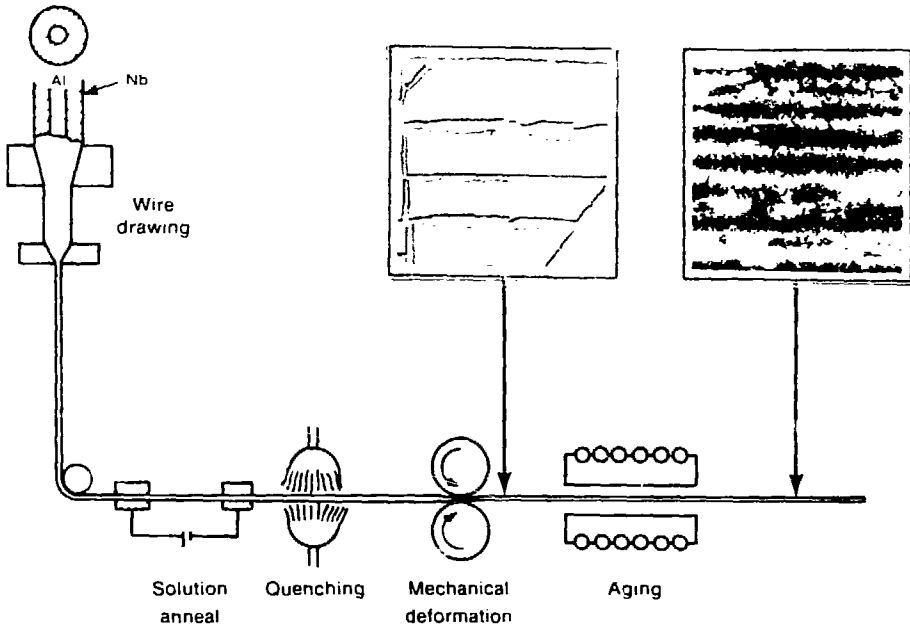


Figure 1. A Quench-Age process for the fabrication of Nb(Al) superconductors.

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to what was expected, the saturated solid solution has only limited ductility at room temperature, in the order of 7 percent reduction in thickness. Although it was found that the ductility can be doubled by working the material at 400 C, all indications suggest that extensive mechanical deformation of the solid solution cannot be readily performed. However, moderate deformation of the solid solution results in the formation of a network of twins as shown in the left photomicrograph of Fig. 1. These twins act as very effective sites for nucleating the Al₅ phase during aging, as shown in the photomicrograph to the right. Thus, an in situ multifilamentary morphology may be achieved.

The critical temperature of 3 samples which had been solution quenched and aged for 1 hour at 1000 C, 18 hours at 950 C and 24 hours at 900 C were measured inductively through the cooperation of Dr. R. Hammond and the Stanford University Department of Applied Physics. The onset of superconductivity for the samples was 17.6 ± 0.5 K with a transition width of about 1 K. Although there was a 100 C difference in aging temperature, no detectable

difference in T_C was observed. This value of T_C is a full 2 K higher than has been previously reported for Nb_3Al formed at temperatures below 1000 C.

POWDER METALLURGY TECHNIQUES

Prealloyed powders (Nb_3Sn and $Nb_3(Al,Ge)$)

In any processing sequence that involves the formation of the A15 phase by a diffusion controlled reaction there is always the question of achieving optimal stoichiometry. It was thought that this important question could be circumvented by preparing, as a first step, a prealloyed powder having precisely the desired stoichiometry. A process of this type, if successful, would have tremendous versatility. Not only would it be applicable to any binary system, regardless of the individual properties of the component elements, but also to ternary systems where the diffusion reactions are far more complex. The niobium-tin system was selected for the first feasibility assessments.

Niobium and tin powders of -325 mesh size were thoroughly blended in a proportion corresponding to Nb_3Sn . The powder mix was compacted in a steel die and then sintered at 1800 C for 1/2 hour. Metallographic and x-ray analysis showed the compact to be more than 95 percent Nb_3Sn . The compact was then pulverized and ground to a -400 mesh prealloyed powder. Niobium, copper and monel tubes were used to jacket the powder. As one example, a powder filled niobium tube was encased in a copper tube. The assembly was wire drawn to a convenient diameter and then cut into a number of lengths which were bundled in another copper tube. This procedure was repeated to a point where a wire was obtained that had an outside diameter of 0.030 inches and which contained 70 consolidated powder cores. A metallographic examination of a cross section showed the cores to be apparently well bonded. However, measurements of the current carrying capacity were disappointing. It was surmised that there must be a lack of true metallurgical bonding between the powder particles. Another set of samples was prepared that had been heat treated for 1 hour at 900 C. No significant improvement was observed. It was therefore decided to perform a systematic study of particle bonding in an A15 compound.⁵

The niobium-aluminum-germanium system was selected for this investigation. Niobium, aluminum and germanium powders were weighed out to a nominal composition of 75 at. percent niobium, 18.75 at. percent aluminum and 6.25 at. percent germanium. After thorough blending, the powder was pressed at 40 ksi in the form of small rectangular compacts. These compacts were arc melted in water cooled copper crucibles under an argon atmosphere, using a tungsten electrode. Allowances were made

when formulating the alloys to compensate for a small weight loss, attributable mainly to evaporation of aluminum during melting. The melted compacts were inverted and remelted four times to ensure complete fusion and improved homogeneity. The arc melted buttons were further homogenized by heating at 1840 C for 2 hours in an argon atmosphere.

Phase identification by metallography was facilitated by anodizing for five minutes in a 10 wt.% solution of citric acid at 25 volts. The characteristic colors of the four possible phases that could occur are: Niobium solid solution (blue-green); A15 phase (gray-purple); and two minor solute rich phases (pink and orange).⁶ The sample consisted of more than 95 percent homogeneous A15 phase, and less than 5 percent of solute rich phases which were present mainly at the grain boundaries. The homogenized arc melted buttons were crushed and then milled in a planetary grinder. X-ray diffraction analysis of the powder confirmed the metallographic findings. The -400 mesh fraction of this powder was used for the particle bonding studies.

The first procedure investigated was cold isostatic pressing followed by sintering. Rubber molds containing the powder were immersed in an oil bath which was pressurized to 60 ksi for 2 minutes. Compacts were sintered in a helium atmosphere for 1 hour over the temperature range 950-1650 C. Density measurements were made using the water displacement technique. Accurate volume determination was facilitated by vacuum impregnation of the compacts with epoxy. The density of an homogenized arc melted button was found to be 7.72 g/cm³, and this value was taken to be the theoretical density. The relative densities reported are the ratio of the measured density to the theoretical density. The microstructures were in good conformity with the density measurements.

It appears from both the density measurements and the photomicrographs that the driving forces for sintering are insufficient to achieve observable densification of the A15 compacts at temperatures up to 1550 C. Only at about 1650 C does the first stage of sintering begin, with a small increase in the connectivity of the powder particles. Increasing the compacting pressure or lengthening the sintering period had little effect. A number of additives were tried in an attempt to activate the sintering process. Even with copper, the most effective of the additives tried, only 75-80 percent of the theoretical density could be obtained.

Hence, it may be concluded that the conventional pressing and sintering technique is ineffective for densification of A15 powder. This may well be the principal reason for the poor

superconducting properties exhibited by wires containing cores of precompounded Nb_3Sn .

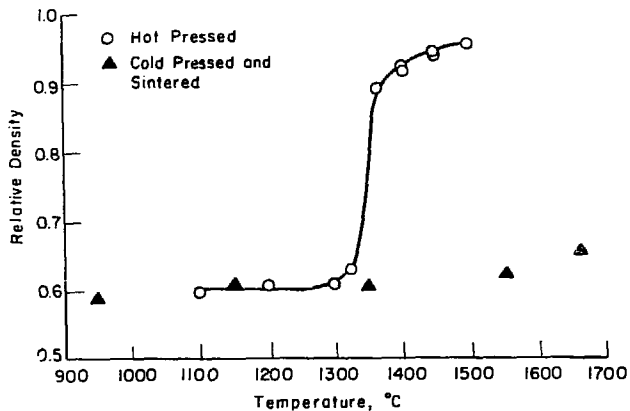
To further elucidate this approach, it was decided to investigate the simultaneous application of heat and pressure, via hot pressing. The hot press employed was designed and constructed at LBL. Essentially, it consists of a water cooled stainless steel chamber containing an externally controlled revolving platform which accommodates 8 graphite die assemblies. Thus eight pressings can be made without breaking the vacuum or waiting for the cool down of individual assemblies. The heating unit surrounding the die being pressed can be raised and lowered by an externally controlled mechanism, thus permitting rotation of the platform. Hot pressing was done in a vacuum of $5 \times 10^{-5}\text{mm}$ of Hg with an applied pressure of 6000 psi. The same $\text{Nb}_3(\text{Al},\text{Ge})$ powder used in the press and sinter experiments was employed for the hot pressing study. Samples were held under pressure for 1/2 hour at selected temperatures: 1100, 1200, 1300, 1325, 1370, 1400, 1450 and 1550 C.

The densification data for both the hot pressed and the cold pressed and sintered samples are shown in Fig. 2. The contrast in the two modes of processing is quite remarkable. Porosity was substantially eliminated by hot pressing at approximately 1400 C, whereas very little reduction in porosity was observed for cold pressed samples that had been sintered at temperatures as high as 1650 C.

The pressure of 6000 psi used for hot pressing is close to the maximum that can be applied due to the mechanical properties of graphite. With this limitation, the onset of plasticity occurs at 0.76 of the absolute melting point. It is very possible that this value can be significantly reduced by the use of higher pressures. It is intended to further explore the potential of using precompounded powders in the following manner. Wires would be prepared containing one or many cores of precompounded powder. After completion of all the mechanical processing, the wire would be subjected to hot isostatic pressing (HIP). No die would be required, and much higher pressures could be employed. Such a procedure, if successful, would be applicable to other brittle superconducting compounds, provided that they are thermodynamically stable at the HIP temperature required for full densification.

The Infiltration Process for Tapes (Nb_3Sn)

The infiltration process was applied first to the niobium-tin system because of the attention it has received in the literature. It was considered that the availability of extensive data on the superconducting properties of niobium-tin conductors made



XBL 7512-9464

Figure 2. Temperature dependence of the relative density of $Nb_3(Al,Ge)$ compacts for both hot pressed and cold pressed and sintered samples. XBL 7512 9464

by other processes would facilitate the assessment of the merits of a new approach. Since this is a diffusion controlled process it is helpful to consider the equilibrium phase relationships. The desired superconducting phase is the intermetallic compound Nb_3Sn which has the A15 crystal structure. There are two additional intermetallic compounds, Nb_6Sn_5 and $NbSn_2$. Neither of them is of interest for superconductivity, since their critical temperatures are in the order of 2 K compared with 18.1 K for Nb_3Sn . Like Nb_3Sn , both of these phases are brittle. Of particular relevance is the fact that both are unstable at temperatures above approximately 930 C. To avoid them, the diffusion treatments were therefore carried out in the temperature range 950-1000 C.

The first application of the infiltration process was the preparation of a flexible tape^{7,8,9} that could be wound to form solenoids after all processing operations had been completed. The morphology of the tape is that of a composite, with the brittle Nb_3Sn phase in the form of thin, multiply connected

filaments arrayed in a ductile niobium matrix. The filaments have a thickness of 5 microns or less.

To obtain this composite, niobium powder was roll-compacted and sintered to produce a tape that was permeated by a capillary system of interconnected pores. The porous tape was then infiltrated with molten tin in such a manner that all of the pores were completely filled with tin. Although a diffusion heat treatment at this stage produced the desired Nb_3Sn phase, it was found preferable to subject the infiltrated tape to a substantial reduction in thickness by cold rolling prior to the heat treatment. With this sequence a greater volume fraction and a more desirable morphology of the superconducting phase was obtained.

The niobium powder used throughout the development phase of this program was supplied by the Teledyne Wah Chang Albany Corporation. It was produced by the hydride-dehydride process from slabs of electron beam melted ingots. Its chemical composition, in parts per million, was as follows: 1780, oxygen; 380 tantalum; 230 iron; 110 tungsten; and 70 carbon. The as-received powder contained a wide range of particle sizes. A particle size analysis¹⁰ gave the following particle size distribution: 2 w/o -270 + 325 mesh (53-44 μm); 26 w/o -325 + 400 mesh (44-37 μm); and 18 w/o for each of the size fractions -400 + 500 mesh (37-30 μm); -500 + 750 mesh (30-20 μm); -750 + 1000 mesh (20-15 μm) and -1000 mesh (15 μm). Work was done using both the as-received powder and various sharply graded size fractions. A scanning electron microscope study of the powder showed that the particles were angular and highly irregular in shape. A particle shape of this type was an important factor in achieving good green strength in the rolled tape.

The mill used for powder rolling has 2 inch diameter, hardened steel rolls, the axes of which are in a horizontal plane. The mill is powered by a stepless variable speed drive which provides a range of roll speeds from 2 to 20 rpm. Grooves 1/8 inch wide and 1/8 inch deep were ground into the rolls, leaving between the grooves the desired width of rolling surface. Side retainers of 1/8 inch thick plexiglass were machined to fit in the grooves and rest on the reduced roll diameters, thus confining the powder laterally throughout the roll bite. A plexiglass hopper, affixed to the side retainers, has an adjustable slide to regulate the powder flow and maintain an adequately constant powder head. Uniformity of roll compaction was significantly improved by roughening the roll surfaces.

The maximum tape thickness is determined mainly by the roll diameter. The 2 inch diameter rolls employed imposed a maximum

tape thickness of approximately 0.025 inches. Using the as received powder (-270 Mesh), tape with a good surface appearance was produced at roll speeds from 2 to 20 rpm and with roll gaps from 0.010 to 0.018 inches. With a given roll speed, a decrease in roll gap led to a decrease in porosity and an increase in green strength. When the roll gap was held constant, the effect of increasing the roll speed was to diminish the green strength and increase the porosity. A good balance between green strength and porosity was obtained under the following conditions: roll speed, 5 rpm; roll gap, 0.016 inches. The green tape, with a thickness of 0.022 inches, had a porosity of about 30 percent and could support 830 inches of its own weight.

The sintering temperature and time period were constrained to a rather narrow range by the simultaneous requirement of ductility and porosity. A practical compromise was achieved by sintering for 3 minutes at 2250 C in a vacuum of 4×10^{-5} Torr. The tape thus processed had a porosity of about 25 percent and could sustain a bend of 0.1 inch radius.

Infiltration was accomplished by immersion of the sintered tape for one minute in a tin bath maintained at a temperature of 850 C. Although infiltration can be carried out successfully at temperatures as low as 350 C, problems were encountered in the cold rolling of the infiltrated tape. Because of the low flow stress of pure tin, some of it was squeezed out during the mechanical deformation, and this tin loss reduced the volume fraction of Nb_3Sn in the final product. Several methods were investigated for preventing the loss of tin. The simplest and most effective procedure was based on considerations relating to phase equilibria in the niobium-tin system. After infiltrating at temperatures in the range of 350-850 C, it is thermodynamically possible to have niobium, Nb_3Sn , Sb_6Sn_5 , $NbSn_2$ and tin all present in the as infiltrated tape. Nevertheless, the reaction kinetics at the lower temperatures for the short immersion times employed (one minute) are such that only niobium and tin are metallographically visible. Increasing the infiltration temperature to 850 C, however, produces a marked change in the reaction kinetics. A significant amount of Nb_6Sn_5 , which is readily distinguished under the microscope by the characteristic reddish brown color imparted by anodic etching, is now present. It occurs as a dispersed phase and sufficiently hardens the tin to prevent any loss during the deformation. Thus, the maximum volume fraction of Nb_3Sn realizable from the amount of infiltrated tin is achieved.

As mentioned earlier, a diffusion reaction heat treatment, at temperatures above 930 C, carried out on the as infiltrated tape does produce Nb_3Sn . However, there are marked disadvantages in doing so. Since the diffusion path is long (1/2 the

original pore size), an extended reaction time is required to involve all of the tin. Moreover, an undesirable morphology is obtained. For example, an infiltrated sample was heat treated for 16 hours at 1000 C. There was still some unreacted tin and the Nb₃Sn occurred in massive form with the result that the heat treated tape was extremely brittle and could be handled only with the utmost care.

Interposing a deformation by cold rolling after infiltration and before the heat treatment resulted in dramatic improvements. As the amount of deformation is increased the tin becomes elongated to a filamentary morphology, resulting in several benefits. The greatly increased interfacial area between the niobium and tin reduced the time for complete reaction of the tin from more than 20 hours to a few minutes. As pointed out earlier, a filamentary structure is desirable for conductor stability. The filamentary structure also provides the tape flexibility required for coil winding. An appropriate morphology was obtained by cold rolling the infiltrated tape to a reduction in thickness of 75-85 percent.

The diffusion reaction can be carried out in the temperature range of 930-1350 C. However, the current carrying capacity degrades rapidly as the reaction temperature exceeds 1000 C. It is in fact desirable from the standpoint of grain size to carry out the reaction at as low a temperature as practicable. The tapes are normally heated for 3 minutes at 950-975 C.

The completed tapes exhibit high values for the important superconducting parameters: a critical temperature of 18.1 K, and an overall current carrying capacity, at 4.2 K, close to 10⁵ amp/cm² in an applied field of 10 tesla. The current carrying capacity was determined for a sample that had been formed into a coil of 0.5 inch radius. After testing, the sample was unsoldered from the contacts, uncoiled and then reverse coiled to the same diameter. A retest showed virtually no deterioration in superconducting properties.

The tapes have, however, a less than optimum filament morphology. Typically, the filaments have a cross section of 30 microns in width and 5 microns in thickness. According to the stability criteria discussed previously, no dimension in a filament section should exceed 10 microns. In the powder rolling process there is little control over the filament width, which is directly related to the original pore size. It was decided, therefore, to modify the process so that the conductor could be made in wire form. Wire would provide an additional advantage besides improved stability. Suitably clad, a single wire can be used as the basic element of a flexible multicore conductor or a multistrand cable to carry large currents.

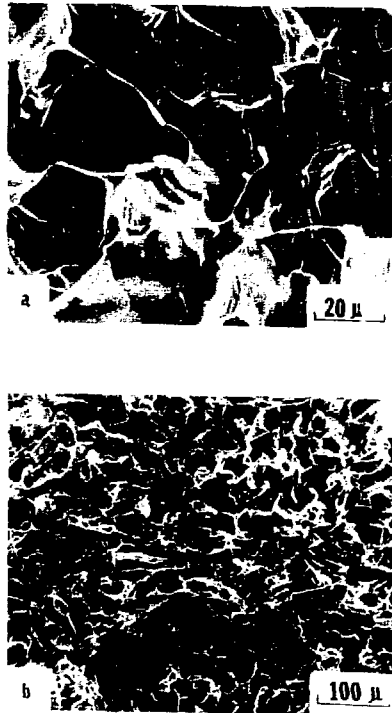
The Infiltration Process for Wire (Nb_3Sn)

For producing wire, the concept of infiltrating a porous niobium form was retained, since the results were highly satisfactory. The powder rolling step, however, had to be replaced by a more appropriate mode of powder compaction. Two variations of pressureless sintering¹ were tried. Although successful, this approach was abandoned in favor of cold isostatic pressing which proved far more convenient.

Niobium powder with a sieve range of $-250 + 400$ mesh was isostatically compacted in rubber molds at a pressure of 207 N/mm^2 (30,000 psi) to produce rods. Vacuum sintering at 2250 C provided the desired combination of porosity and ductility. In order to control the level of interstitials, especially oxygen, the time at sintering temperature depends on the mass of the rod. For the small diameter rods ($3/16$ inch) intended for laboratory use, a sintering time of 30-60 minutes was satisfactory. A scanning electron micrograph, Fig. 3, shows clearly the ductile niobium matrix and the system of interconnected pores.

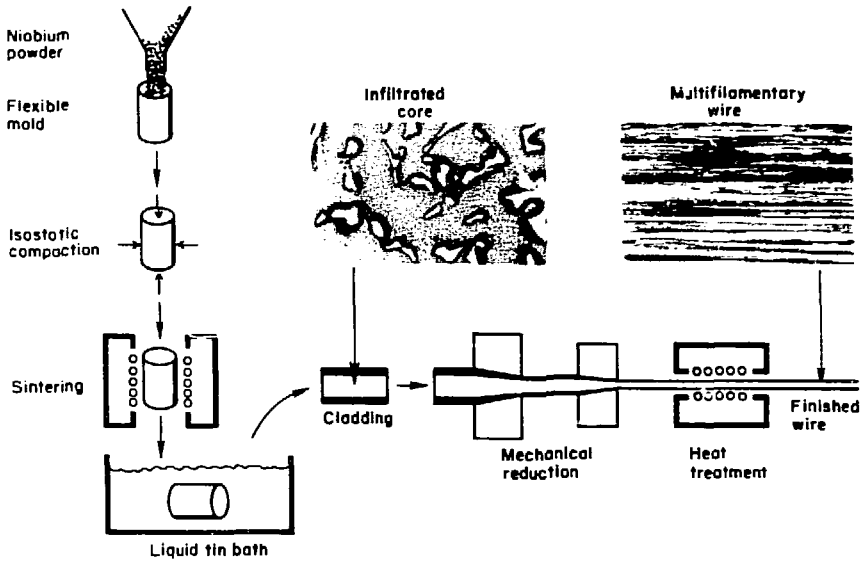
For infiltration, the sintered rods were immersed in a tin bath maintained at a temperature in the range of $350-400 \text{ C}$. These lower temperatures were preferred in order to prevent the formation of brittle intermediate phases which could impair the ductility of the composite. At this point a cladding of one or more metals is applied to the infiltrated rod to accomplish several purposes. An exterior cladding of monel, for example, greatly facilitates wire drawing. An inner jacket of tantalum, in principle, serves as a diffusion barrier to prevent undesired reactions between the infiltrated core and the exterior jacket. Fortunately, as a result of the very short reaction times required in the infiltration process, it was found that the diffusion barrier could be eliminated with no adverse effects, thus greatly simplifying the procedure.

The composite rods were mechanically reduced to fine wire by a combination of form rolling and wire drawing. Indicative of the ductility achieved, a reduction ratio in cross sectional area of 4000:1 was consistently obtained. Heat treating the wire for 2-3 minutes at 950 C results in all of the tin reacting with niobium to produce multiply connected filaments of the superconducting compound, Nb_3Sn . The filaments are well within the desired size range for adiabatic stability, having transverse dimensions of the order of 1 micron. A schematic representation of the entire process is shown in Fig. 4.



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Figure 3. Scanning electron micrograph of porous niobium rod sintered for 30 minutes at 2250°C.



THE INFILTRATION PROCESS FOR PRODUCING MULTIFILAMENTARY SUPERCONDUCTING WIRE

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Figure 4.

Properties of Wire made by the Infiltration Process

The critical temperature, taken as the midpoint of the inductance change during the transition from the superconducting to the normal state, is 18 K. This value remains substantially constant for reaction temperatures from 900 to 1200 C. Data from both pulsed (rise time, 8 milliseconds) and steady field measurements were used to determine the dependence of the critical current density on the applied magnetic field.¹² The area used in the computations was that of the entire cross section of the Nb-Nb₃Sn core. Steady field data were obtained through the courtesy of the Accelerator and Fusion Research Division of the Lawrence Berkeley Laboratory, the Brookhaven National Laboratory and the Francis Bitter National Magnet Laboratory (M.I.T.). They were determined at a resistivity of 10^{-12} Ω -cm. The results (Fig. 5) show good agreement between the two sets of data at high fields, but lower values for the pulsed field determinations at fields below 5 tesla. This discrepancy is attributed to Joule heating at the current contacts of the very short samples used in the pulsed field tests. To further elucidate the current carrying capacity at very high fields, steady field tests were made recently at the Francis Bitter National Magnet Laboratory over the range from 17 to 22 tesla. The data points fell smoothly along the steady field curve of Fig. 5. The critical density was 1×10^4 amps/cm² at 20 tesla and 4×10^3 amps/cm² at 21 tesla. Wires made by this process appear to be especially suitable for applications requiring fields of the order of 15 tesla. In another series of tests, it was found that the critical current density increases with decreasing filament size down to 1 micron, below which there appears to be a diminishing effect. The minimum diameter to which the reacted wires can be bent with no degradation of the critical current density is 2 cm. Here too, there is an effect of filament size and it is anticipated that with finer filaments even smaller bend diameters can be tolerated.

POROUS NIOBIUM RODS FROM POLYMER COATED POWDER

The infiltrated rods used for most of the laboratory studies just described had a diameter of 5 mm. In order to produce long lengths of superconducting wire, the diameter of the isostatically pressed compacts would have to be increased substantially. Concomitant with the studies of the size effect, it was decided to investigate an alternative approach^{13,14,15,16} that could produce indeterminate lengths of a given diameter.

The particles of niobium powder were coated with a layer of the thermoplastic, polystyrene. The polymer content was varied

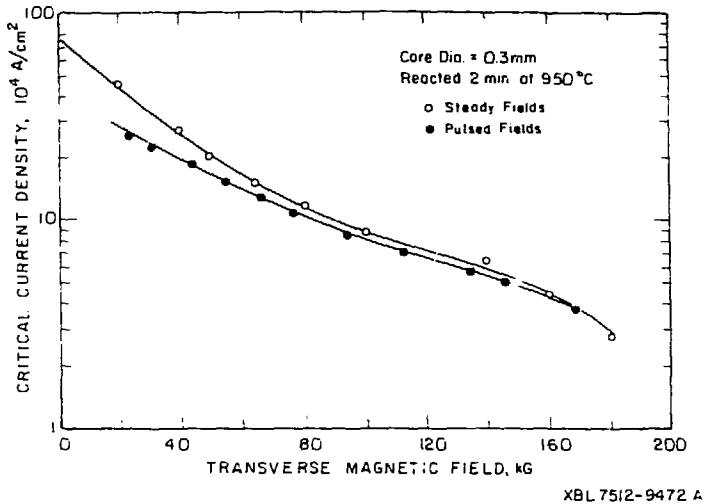


Figure 5. Critical current density of the Nb-Nb₃Sn core as a function of the magnetic field under pulsed and steady field conditions. XBL 7512 9472A

from 7.5 to 10 percent by weight. A significant result was the fact that the coating imparted to the polymer-metal powder mixture the characteristics of a thermoplastic, and conventional plastic forming methods such as extrusion could be performed readily. It was found that plasticizing the polymer by the addition, in the amount of 1/5 of its weight, of the eutectic mixture of diphenyl and diphenyl ether not only reduced the required extrusion pressure, but also assured consistent extrudability.

The polymer coated niobium was heated to 165 C and extruded through a 0.48 cm (3/16 inch) diameter orifice. The extrusion pressure varied from 27,000 psi for a 7.5 w/o polymer content to 7000 psi for a 10 w/o polymer content. After cooling to ambient temperature, both the surface finish and strength of the extruded rods were quite satisfactory. Samples were then subjected to a programmed heating cycle. During a dwell period at 400 C the polymer was completely expelled by volatilization. Although the shape was undistorted, the strength at this stage was virtually

nil. However, after increasing the temperature to 1350 C, the strength was more than adequate for any handling required prior to final sintering. After sintering, the infiltration, mechanical deformation and diffusion heat treatment were carried out as described in the previous section. The residual porosity after sintering varies nearly linearly with the w/o of polystyrene in the polymer-metal powder mixture. The porosity was approximately 25 percent for a 7.5 w/o polymer content and about 40 percent for a 10 w/o polymer content.

A15 TERNARY COMPOUNDS

Nb₃(Al,Ge)

The A15 ternary compounds offer high promise for substantial improvement of the superconducting properties over the presently practical conductors, like Nb₃Sn and V₃Ga. Of the stable superconductors with high critical temperatures the ternary compound Nb₃(Al,Ge) has the highest critical field. It was reported to possess a T_c of 20.7K^{17,18} and an H_c of about 4i tesla.¹⁹

Nb₃(Al,Ge) has received significant attention since its discovery by Matthias et al.¹⁷ For a variety of reasons, associated with the phase relationships and inherent mechanical properties difficulties were encountered in preparing Nb₃(Al,Ge) in the form of a flexible multifilamentary conductor. Several methods of preparation have been reported in the literature.²⁰⁻²⁴ The sputtering process yields promising qualities in terms of the current carrying capacity,²⁰ but this approach is limited by the relatively low rate of deposition. Feasibility of the powder metallurgy process for producing tape of Nb₃Al_{0.75}Ge_{0.25} has been demonstrated.²¹ The Kunzler technique was used whereby powders of Nb, Al and Ge were mixed in the appropriate proportions, sealed in a cupronickel tube and cold worked by swaging and rolling. The tape was subsequently reacted to form the A15 compound. The critical current densities, in steady transverse magnetic fields of 15 tesla, were found to be about 10⁴ amp cm⁻².

An investigation was undertaken at Lawrence Berkeley Laboratory⁵ to evaluate the factors affecting densification of precompounded powder of Nb₃(Al,Ge). This study has been already described in the present paper. The salient feature of the results was that a hot pressing process, of 6000 psi at 1400 C, substantially eliminates the porosity. It can further be assumed that by application of higher hydrostatic pressures the temperature for plastic flow could be reduced below 1000C. Considerable plastic flow, at ambient temperature, was observed

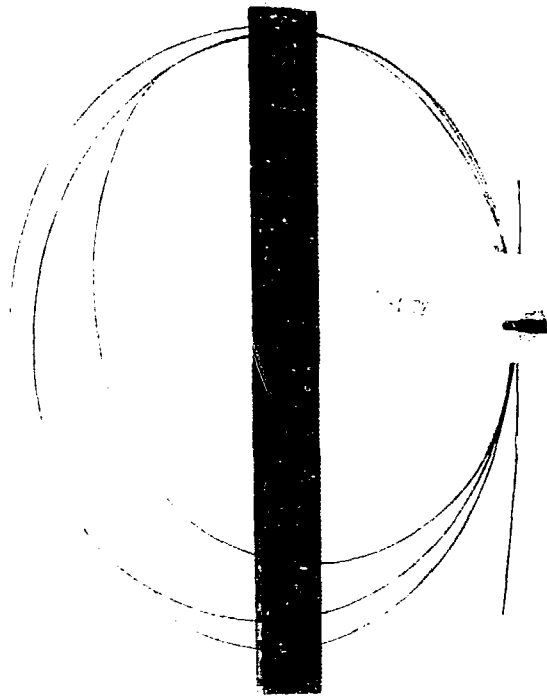
in samples of V_3Ga in response to high pressure in the 3000 ksi range.²⁵

The infiltration route was adopted in order to obtain a relatively ductile material that can be mechanically deformed into a fine wire, containing an interconnected network of filaments of the order of a few microns in diameter. Subsequently a diffusion heat treatment was applied in order to convert these filaments into $Al_5 Nb_3(Al,Ge)$.

Additional advantages of the infiltration process are due to the fact that the composition of the infiltrant (Al-Ge or Al-Si alloys and eutectics) can be readily controlled. Appropriately programmed diffusional anneals may form the desired composition and microstructure of the compound. Moreover, an optimized thermomechanical process may yield the desired combination of high critical current density and critical temperature. This objective can be achieved by appropriate control of the grain size and long range ordering, and by determining conditions for the approach to optimal stoichiometry.

The Al-Ge system forms a low melting point eutectic (424 C) at the composition of 70 percent Al - 30 percent Ge. The inherent brittleness of the Al-Ge eutectic requires particular attention as to the temperature of the infiltrating bath, the temperature difference between the porous sintered niobium rod and the bath, and the rate of infiltration. The formability of the Al-Ge eutectic, entrapped and solidified within the pore volume, during form rolling or wire drawing can be significantly improved through the application of superplasticity principles.²⁶ Superplastic behavior requires a fine duplex microstructure which is stable at the deformation temperature. The ductility of the Al-Ge alloy confined in a network of pores in the niobium matrix was investigated.²⁷ In the bulk eutectic a lamellar structure was associated with extreme brittleness, whereas when confined in a pore undergoing the controlled cooling regime of the infiltrated rod, e.g., directional solidification or quenching, the composite after infiltration yielded relatively ductile microstructures. Two desirable morphologies of the solidified eutectic were observed--spheroidized particles and a fine lamellar structure. An infiltrated niobium rod containing Al-Ge eutectic of such morphology can be plastically deformed into fine multifilamentary wire, as shown in Fig. 6.

The Al-Ge eutectic was prepared by induction melting the constituent mixture of the exact eutectic composition under an argon atmosphere and casting in a copper-chilled mold. The molten eutectic bath was maintained at about 600 C during immersion. A close temperature control is necessary in order to prevent freezing of the eutectic in the outer pores of the



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Figure 6. Nb-Al-Ge multifilamentary wire of 0.18 mm diameter.

sintered rod and thus blocking further infiltration. The helium gas pressure above the molten eutectic, the immersion time, and the rate of cooling of the infiltrated rod to the ambient temperature are important parameters. They depend on the pore size and shape, viscosity of the eutectic and the desired microstructure of the solidified eutectic in order to assure good formability. Furthermore, the infiltration temperature should be maintained at a practical minimum so as to avoid, at this stage, any diffusion reaction between the eutectic and the niobium.²⁸ At higher infiltration temperatures, and with excess Al in the eutectic bath, there is a tendency towards formation of an Al-solid solution and an Al-rich intermetallic phase $Nb(Al,Ge)_3$. It was found that this intermetallic phase nucleates and grows at relatively low temperatures.²⁹ Holding an infiltrated rod for 12 h at 400 C resulted in complete conversion of the eutectic into $Nb(Al,Ge)_3$. These phases are brittle and have, therefore, a detrimental effect during the subsequent plastic deformation of the infiltrated composite.

The kinetics of the Al₅Nb₃(Al,Ge) phase formation was investigated over a wide range of temperatures (1250-1700 C), reaction times (15-900 sec) and postreaction anneals.²⁸⁻³¹ Data are presented in Table II, for the critical temperatures of Nb₃(Al,Ge) after various heat treatments.

The multifilamentary superconducting Al₅ phase is formed as a result of a diffusion reaction. Its microstructure and superconductive properties are determined by the reaction kinetics. It was found³⁰ that the Al₅ phase grows rapidly during the early stages of the reaction. The growth rate depends on the reaction temperature. In the early stages of the reaction at 1700 C for different phases coexist: the Ge-rich, the Al-rich, the Al₅Nb₃(Al,Ge) and the A₂ phase which is a Nb solid solution. The Ge-rich phase forms the innermost layer of the pore content. Al-rich sigma phase and the superconducting Al₅ phase. These three phases are embedded in the Nb solid solution matrix.

Table II. Critical temperature of Nb-Nb₃(Al,Ge) multifilamentary superconductors.

Reaction Anneal		Postreaction Anneal		T _c (°K)
Temp. (°C)	Time (sec)	Temp. (°C)	Time (h)	
1250	60	750	96	17.2
1300	30	750	96	17.2
1300	30	750	96	17.5
1300	30	750	250	17.4
1300	60	***	***	15.6
1300	60	750	48	16.3
1300	900	***	***	15.4
1400	30	750	96	18.2
1500	30	750	96	18.5
1600	15	750	96	19.1
1700	15	750	96	18.7
1700	60	***	***	17.4
1700	60	750	48	18.7
1700	60	750	96	16.8

As the reaction proceeds, the Al-rich phase gradually transforms into A15. After 15 minutes nolding time at 1700C the Ge-rich phase transforms also, leaving the A15 in a matrix of Nb solid solution. However, all four phases were found to exist after one hour reaction at 1300C.³⁰ The generally observed trend of higher T_c for higher reaction temperatures²⁹ (Table II) may suggest that the presence of either one or both Ge-rich and Al-rich phases, in the specimens reacted at lower temperatures, may cause a reduction in the critical temperature. However, if this were the case, one would expect an increase in the critical temperature with an increase in the reaction time. Such a behavior was not observed.²⁹ The reason for this apparent inconsistency may be due to deviation from the optimal stoichiometric composition with increased diffusion times. The present data indicate that high reaction temperatures and short reaction times improve the T_c value. Figure 7 shows the results of the current carrying capacity of $Nb_3(Al,Ge)$ samples, prepared by different procedures.

In contrast to the behavior of T_c with respect to reaction times and temperatures, the critical current density J_c is significantly improved by decreasing the temperature of the reaction anneal and its duration.²⁹ But this effect is diminished in absolute terms, by the reduced volume fraction of the A15 phase formed under these conditions. An additional negative contribution to the reduced critical current density in the high temperature reaction anneals is due to the excessive grain growth at the elevated temperatures. Grain growth causes a significant reduction in the number of pinning centers, thus reducing J_c .

The full potential of the ternary A15 $Nb_3(Al,Ge)$ for the preparation of flexible multifilamentary stable superconductors can be realized by controlling the kinetic conditions of the diffusion reaction with the purpose of obtaining an optimal combination of T_c and J_c . The problem of formability, for the fabrication of long lengths of multifilamentary conductor, was shown to be soluble by applying suitable thermomechanical procedures.

$Nb_3(Al,Si)$

The infiltration process was applied for the preparation of flexible, multifilamentary superconducting $Nb_3(Al,Si)$ wire.^{32,33} The infiltrant employed in the preparation of $Nb + Nb_3(Al,Si)$ is the binary Al-Si eutectic with a melting point of 577C. The structure and properties of this eutectic have been reported in the literature.³⁴ Al-Si eutectic exhibits poor ductility, but the ductility can be substantially improved by unidirectional solidification of the eutectic. Care

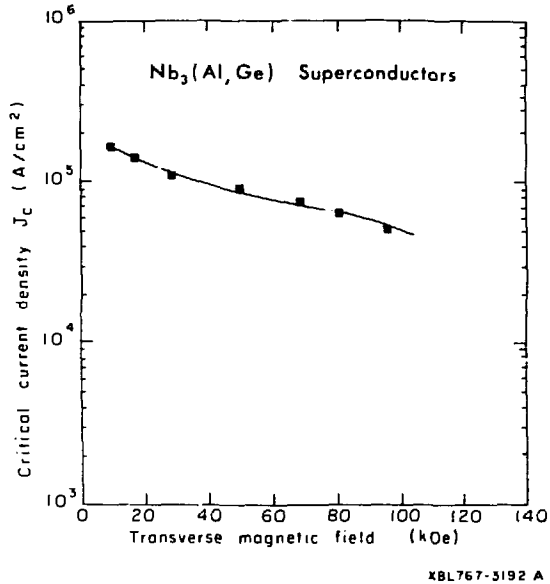


Figure 7. Variation of the critical current density with magnetic field of Nb₃(Al,Ge). XBL 767-3192A

was therefore exercised to slowly cool, unidirectionally, the infiltrated sintered niobium rod. Similar to the procedure adopted for the Al-Ge eutectic described before, the immersion time and temperature for the Al-Si eutectic had to be optimized in order to prevent formation of brittle intermetallic phases that reduce the ductility of the infiltrated composite. The optimal immersion temperature and time were found to be 580C and 30 seconds, respectively. This temperature is only 3C above the melting point of the eutectic. Therefore, the temperature of the sintered niobium rod had to be closely controlled in order to assure complete infiltration.

One major advantage of the Nb-Al-Si system is the ease with which it reduces to wire. Infiltrated Nb rods of 5mm in diameter were easily reduced to 0.150 mm diameter wire at room temperature. The average filament size was found to be about 1 micron. The extremely fine filamentary microstructure achieved with the Nb-Al-Si system allows the formation of A15 at reaction temperatures as low as 850C.

The most favorable diffusional anneal for the formation of $\text{Al}_5\text{Nb}_3(\text{Al},\text{Si})$ was carried out in two stages.³³ The Al-Si eutectic in the form of elongated interconnected fine filaments will readily melt and react at Al_5 reaction temperatures above 1000C. Therefore, a two stage procedure was adopted by which formation of an intermediate compound prevents migration of the Al-Si eutectic.

- a) Primary heat treatment: After infiltration, the niobium rod was held for 1 hour at 650C in order to form, by a diffusional process, an intermetallic barrier around the pores, or elongated filaments. It was found that the composition of the barrier corresponds with the region of NbAl_3 in the Nb-Al phase diagram. This phase is very stable at 650C.
- b) Secondary heat treatment: Following the primary heat treatment, the specimen was heated to temperatures in the range of 1000-1700C for the Al_5 formation. The appropriate holding time at 1700C was found to be 30 seconds. During the secondary heat treatment Al diffuses and reacts with Nb and Si to form $\text{Nb}_3(\text{Al},\text{Si})$. This compound is very stable at 750C. Its composition remains unchanged after 96 hours of annealing at this temperature. Longer holding times at low reaction temperatures, below 1000C, resulted in extremely thin layers of the Al_5 compound.

The highest T_c value for $\text{Nb}_3(\text{Al},\text{Si})$, thus far obtained in flexible wire samples, was 18.8K. The reaction occurred at a temperature of 1700C for 30 seconds, followed by an annealing heat treatment for 96 hours at 750C. This post heat treatment proved to be beneficial for improving the T_c value.

In conclusion, the present paper demonstrates the applicability of the infiltration process to prepare multifilamentary superconductors based on both binary and ternary Al_5 compounds, and indicates that for the ternaries in-depth studies of the reaction kinetics are required in order to realize their full potential.

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