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FORMATION OF Nb_3Al IN POWDER PROCESSED Nb-Al SUPERCONDUCTORS

P.E. Johnson
(M.S. Thesis)

May 1987

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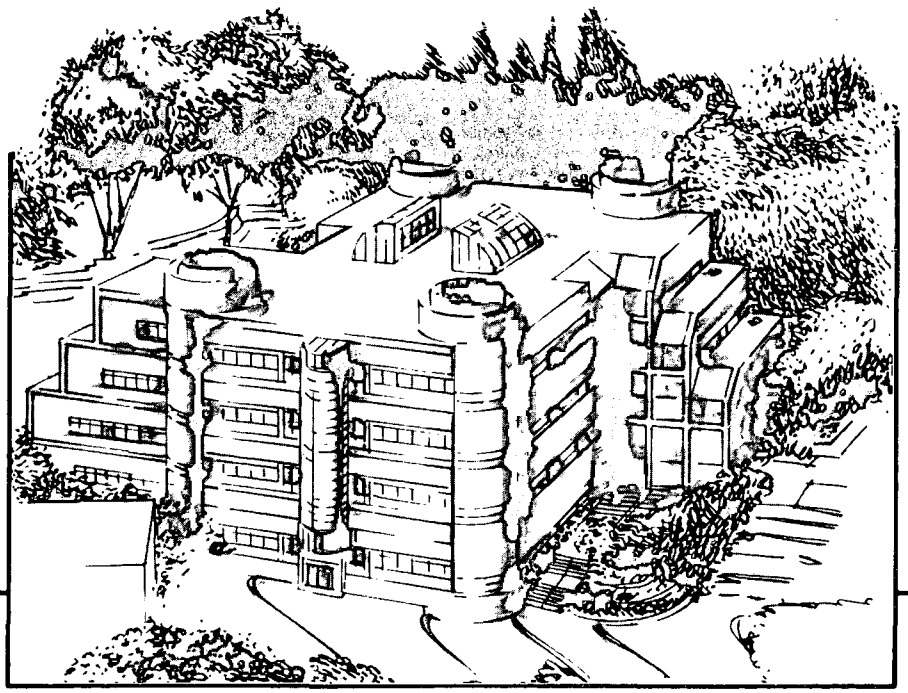

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Formation of Nb_3Al in Powder Processed Nb–Al Superconductors

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FORMATION OF NB_3AL IN POWDER PROCESSED NB-AL SUPERCONDUCTORS

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I. INTRODUCTION

Operation of magnetically confined plasma fusion reactors will require high (12-20 Tesla) magnetic fields. Superconducting magnet windings will be needed to minimize the power input. The development of fusion reactors has therefore accelerated the development of advanced superconductors able to carry high currents in high magnetic fields. Nb_3Al is a candidate for this type of use. Nb_3Al has the A15 crystal structure and an upper critical field (H_{C_2}) of 30 Tesla at 4.2K. This is well above the upper critical field of the superconductors currently in commercial use: Nb_3Sn (H_{C_2}= 24 Tesla), and NbTi (H_{C_2}= 19 Tesla). Nb_3Al is also capable of carrying high current densities in high magnetic fields.

Like other superconductors with the A15 crystal structure, Nb_3Al is a brittle intermetallic phase and cannot be drawn into wire. In powder-processed (P/M) wires, this problem is overcome by using elemental Nb and Al powders which co-deform well. The powders are mixed and compacted into a Monel or copper tube, swaged and drawn to area reduction ratios of 10,000:1 or higher, and then given a reaction heat treatment to form the superconducting phase.

Processing variables that have been found to affect the current carrying capacity of the wires include the starting powder sizes, overall composition, area reduction ratio, and heat treatment. Although a substantial amount of critical current density data has been generated in the past ten years[1-9], a comprehensive analysis of the data has been lacking, particularly in terms of a fundamental understanding of the reactions which occur.

Stoichiometric Nb_3Al is expected to form at temperatures between 1500°C and 2000°C. However, reaction at these temperatures causes excessive grain growth of the Nb_3Al. Magnetic flux lines penetrating a Type II superconductor such as Nb_3Al are subjected to a Lorentz force when a transport current is passed through the conductor. Maintaining the superconducting state requires the flux lines be pinned by

microstructural defects. As in other superconductors with the A15 crystal structure, the dominant flux pinning source in Nb_3Al is grain boundaries[10,11]. The critical current density is therefore adversely affected by large grain sizes.

A lower reaction temperature (900°C) yields an acceptable A15 (Nb_3Al) grain size but A15 formation at these temperatures is limited, by formation of the nonsuperconducting sigma phase (Nb_2Al). The nature and kinetics of the reaction to Nb_3Al at lower temperatures are poorly understood. Existing studies of this reaction have used methods other than the powder process to produce the Nb_3Al compound. Results of these studies are summarized in the Background section.

The critical current density (J_c) of Nb-Al superconducting wire made by powder process is dependent on the volume fraction of A15 (Nb_3Al), the Nb_3Al grain size, and its stoichiometry and order. The highest critical current densities are obtained when the wire is reacted at temperatures at or above 900°C for only short periods. The optimized heat treatments represent a balance between maximizing the volume fraction of A15 and improving its stoichiometry by formation at higher temperatures, while avoiding excessive grain growth by reacting at lower temperatures. The best of these heat treatments each give approximately the same Nb_3Al grain size. Thus with the processing techniques currently being used, the J_c is predominantly limited by the amount and stoichiometry of the Nb_3Al.

In high magnetic fields, the critical current density is strongly dependent on the upper critical field, which is determined primarily by the stoichiometry of the Nb_3Al[10]. The critical temperature (T_c), like the upper critical field, is considered to be a measure of the "intrinsic" quality of the superconductor, indicating the stoichiometry, order, and strain. If the A15 phase is stoichiometric and well ordered, a high T_c (and high H_{C_2}) is expected, regardless of the volume fraction of superconductor. On the other hand, if sigma phase is present with the A15, the resultant composition gradient across the sigma-A15 interface(s) requires that some of the A15 be off-stoichiometric, and therefore

that the T_c (and H_{C_2}) be low. Thus the extent of the A15 (Nb_3Al) reaction and the quality of the A15 formed are interdependent.

This work focuses on the factors that control the extent of Nb_3Al formation in Nb/Al powder wires. The morphology and content of the reacted and unreacted wires are studied in optical, SEM, and TEM micrographs. Critical current density data and its dependence on processing are explained in terms of the unreacted microstructure and its effect on the extent of Nb_3Al formation. As a method of improving the critical current density, a new variation of the conventional powder process for wire manufacturing is developed and tested.

II. BACKGROUND

The Nb-Al phase diagram[12] is shown in figure 1. Stoichiometric Nb_3Al is expected to form at temperatures above 1500°C, where excessive grain growth degrades the critical current. In addition to the superconducting A15 phase (Nb_3Al), the other compounds which might form when Nb and Al react together are: the sigma phase (Nb_2Al) an Al-rich body-centered tetragonal phase, $NbAl_3$, and a bcc Nb-rich solid solution.

Several non-equilibrium techniques have been used to study Nb_3Al formation at lower temperatures. These usually involve extending the solubility limit of Al in Nb to form a supersaturated Nb-rich solid solution (here designated as NbAl), which is then transformed to A15 (Nb_3Al) from the bcc (NbAl) structure. The equilibrium solubility at 1000°C is well below 25 at. % Al, the composition of stoichiometric Nb_3Al. Although most of these processes will not be feasible for large scale applications such as the windings of a large high field magnet, these studies demonstrate the capabilities of the Nb_3Al compound. They also provide some insight into what conditions are necessary for full reaction to stoichiometric A15 (Nb_3Al), and indicate how the reaction might be proceeding in the powder wires.

In one such study, Wang and Dahlgren[13,14,15] used Nb-Al powder compacts as sputtering sources and high sputtering rates (1 μm/min), to produce 0.1 mm thick Nb-Al deposits at approximately 25 at.% Al. The deposits were removed from their substrates and thin foils were prepared for TEM. Electron diffraction patterns showed that only the bcc (NbAl) phase was initially present in these deposits. After heat treating the samples at 700°C for 24 hours, a complete transformation from bcc (NbAl) to A15 (Nb_3Al) was observed. The highest superconducting critical temperatures (T_c) measured were 17.4K, and small A15 grain sizes (350 Å) were reported. Nb-Al powder wires typically have a T_c of about 16K, and A15 grain sizes of 1000-3000 Å[5,7,16]. Thus the extent of the reaction, the quality of the A15 formed and the A15 grain size can all be improved if a method can be found to produce a homogeneous bcc (NbAl) before the A15 reaction starts.

Kammerdiner and Luo[17] prepared niobium-rich Nb-Al alloys of varying aluminum content by both sputtering and by quenching from the liquid state. Shown by X-ray diffraction data, all of the as- quenched and as-sputtered samples had a bcc (NbAl) structure. Samples from both preparation methods were given an 800°C heat treatment for 2 to 5 days. Critical temperatures and lattice parameters were measured. The best of the quenched specimens showed a slightly higher T_c (18.6K) than the best of the sputtered samples (16.6K). All high T_c samples had X-ray patterns showing A15 (Nb_3Al) phase only. Some of the lower T_c samples showed the presence of sigma phase as well as A15(Nb_3Al).

Webb[18,19] has studied small (1 gm) samples of Nb-Al alloys at 25 at% Al, which were quenched from under a solidus (1900°C). The crystal structure of the as quenched samples was predominantly (97 vol%) bcc (NbAl). The samples were then cold rolled and heat treated at 700°C or 950°C. Complete conversion to A15 (Nb_3Al) occurred after 40 minutes at 950°C. These small samples had critical current densities better than $1X10^5$ A/cm^2 near 20 T. This is more than ten times the highest critical current densities yet reported for Nb-Al wires[4,16].

Lo et al [20] made Nb-Al superconducting tapes by rapid quenching from the liquid state (2500°C), and subsequent annealing at 750°C for 162 hours. The liquid was dropped onto a copper substrate which was rotating at high speeds (2000-5000 rpm), producing estimated cooling rates of 10^5-10^6 °C/sec. In this case, X-ray powder patterns showed the as-quenched tapes to be A15 (Nb_3Al) phase only. An increase in T_c from 16K to 18.4K after annealing was cited as evidence that the 750°C heat treatment was an ordering anneal. High critical current densities were also obtained using this method of fabrication ($1.8X10^6$ A/cm^2 at 15 Tesla).

Tachikawa[21,22] has also studied Nb-Al alloys transformed to A15 (Nb_3Al) from a supersaturated bcc (NbAl) solid solution prepared by rapid liquid quenching. Recently Tachikawa has used continuous, high speed, CO_2 laser beam irradiation to rapidly heat

and cool the material. An 8wt.% Al, Nb-Al powder compact was prepared and cold worked into a 100 mm thick tape. The final critical current densities (of the reacted area) were 2-3 $X10^4$ A/cm^2 at 15T and 4.2K, slightly lower than conventional Nb-Al powder wires. The relatively low critical current densities are at least in part due to an incomplete transformation to A15 (Nb_3Al): X-ray diffraction data showed sigma phase (Nb_2Al) as well as A15 in the reacted tapes.

Bormann[23] recently studied thin Nb/Al multilayers made by sputter deposition onto sapphire substrates. In this case discrete layers of Nb and Al were separately deposited. Two sets of multilayers were prepared, with Nb/Al layer thicknesses of 30/9.2 nm, and 100/30 nm, respectively. Both sets are near stoichiometric proportions for Nb_3Al. X-ray diffraction data was collected during a temperature ramp heat treatment from room temperature to 800°C.

It was found that the thinner multilayers were able to fully react to stoichiometric A15 (Nb_3Al). Intermediate formation of $NbAl_3$ was reported, which decomposed to form a supersaturated bcc (<u>Nb</u>Al) solid solution at 700°C. The A15 phase then nucleated directly from the metastable <u>Nb</u>Al. In Bormann's thicker samples, the reaction to A15 (Nb_3Al) did not go to completion. Off-stoichiometric A15 , sigma phase (Nb_2Al), and unreacted Nb were found. It was proposed that the $NbAl_3$ layer formed was too thick to completely decompose to <u>Nb</u>Al solid solution before the nucleation of A15 began. Presumably the A15 layer then acted as a diffusion barrier, blocking off the remaining Nb from the Al supply. This explanation was not fully verified however, since no microscopy was done on the samples.

For the case of Bormann's temperature ramp heat treatment (50-100°C/20 minutes), all of the aluminum reacted before melting (T_m = 660°C). It is unclear whether this is the case when the Nb and Al are heated directly to around 1000°C, as in the best of the wire heat treatments (the heat treatments which yield the highest J_c). In Bormann's multilayers, the Al went into $NbAl_3$ or into solution in Nb. As the temperature was

increased, more Al was dissolved into Nb, and the A15 phase formed directly from a metastable NbAl solid solution. The presence of liquid Al during the wire heat treatments, and/or its effect on the reaction(s) has not yet been studied.

To summarize, it has been found that the A15 (Nb_3Al) phase can nucleate directly from a supersaturated bcc NbAl solid solution. Such a solid solution can be formed in small "bulk" samples or near a Nb-Al interface when the diffusion distances are well under one micron. Whether this is the only path for the reaction has not been determined, nor have the conditions necessary for the solid solution formation been accurately quantified.

In Nb-Al superconducting wires made by powder process, existing data has always shown that increasing the area reduction of a given wire increases the overall critical current density. Increasing the area reduction ratio will have at least two effects on the unreacted microstructure which might effect the reaction to Nb_3Al: increasing the amount of deformation in the Nb and Al particles, and increasing the amount of Nb/Al interface per unit cross-sectional area in the wire. The best of the wire heat treatments are all above the melting temperature of Al. If the Al is melting before it reacts, its prior deformation is not expected to be a relevant factor in the reaction. A preliminary investigation, described in Appendix A, showed that the amount of deformation in the Nb does not play a significant role either. This suggests that increasing the Nb/Al interface is improving the J_c.

The reacted wires consist of A15 (Nb_3Al), sigma phase (Nb_2Al), and residual (unreacted) Nb. In some very low reduction wires, $NbAl_3$ has also been seen. These phases and their characteristic appearance have previously been identified in TEM[4,5,7,16]. Figure 2 is a TEM micrograph of a longitudinal section of reacted wire. The fine-grained phase in the center, which appears heavily twinned, is Nb_2Al . The larger clear equiaxed grains are Nb_3Al, and the darker, elongated grains are unreacted Nb. In a typical Nb-Al powder wire, the A15 (Nb_3Al) layers vary in width from as little as one grain size (roughly 200 nm) to ten or twelve grains (over 1 μm). Some of the sigma

phase regions are quite large (1.3 micron wide)[16].

It has been proposed that the reaction to A15 (Nb_3Al) in these wires occurs only near the initial Nb/Al interfaces. Increases in J_c with increased reduction are then due to increasing the specific amount of Nb-Al interface, and thereby allowing more A15 to form. Although plausible, this hypothesis has not previously been verified, nor has any quantitative examination of the reacted or unreacted wires been performed. This work is intended to address these issues.

III. EXPERIMENTAL PROCEDURE

LBL powder wires

-Powder/Powder wires

Niobium Hydride powders (-100 +200 mesh, < 500 ppm O) were obtained from Teledyne Wah Chang in Albany, Oregon. The powders were ground in a Tungsten-Carbide ball mill and screened through sieves. A -270 , +400 powder (65 μm) was used. The powders were dehydrided in a vacuum furnace, and finally placed through a particle classifier to remove any fine powders remaining after the dehydride process. Aluminum powder (99.999% purity) was supplied by SPEX of New Jersey. The aluminum powders were passed through a particle classifier three times with a successively finer cut on each pass. This yielded a uniform 20 μm powder. The Nb and Al powders, after processing, are shown in Figures 3a and 3b.

The powders were then weighed, mixed and poured into a Monel sleeve 1" (2.5 cm) OD, 3/4" (1.9 cm) ID, approximately 5 " (12 cm) long. The powder mix was compacted at a pressure of 65 ksi (450 MPa) and an end plug was welded in place. The Monel tube was then swaged to a diameter of approximately 0.2" (0.5 cm), and drawn down to final size. The drawing was stopped at successive stages of reduction. Samples were stopped at area reduction ratios (R) of: 6, 22, 90, 250, 540, 980, 1800, 2500, 7000, and 10,000. A 5 wt% Al wire, at R=10,000 was used for the critical current measurements.

-Precoated Nb powder wire

Niobium powders were prepared as for the Nb/Al powder-powder wires. Approximately 50 gm of loose Nb powder was precoated with aluminum by evaporation. The evaporation chamber was evacuated to 2 x 10^{-5} torr before evaporating. The powders were spread in a 10 " (25 cm) diameter tray. Twenty times during the coating process the chamber was reopened, the Al source replaced, and the powder mixed to ensure a uniform

coating. A 5- wt.% Al precoated powder was used. This was also drawn to area reductions of 10,000:1 for critical current measurements.

Heat treatments

The Monel cladding on the drawn wires was removed with nitric acid before heat treating. Short lengths (4 ") (10 cm) were encapsulated in evacuated quartz tubes backfilled with Argon gas. The following heat treatments were used for the critical current and critical temperature measurements, and for microstructural analysis:

900°C/30 min.
900°C/30 min.+ 750°C/2 days
900°C/30 min.+ 750°C/3 days
1100°C/2 min.+ 750°C/2 days
1100°C/2 min. + 750°C/3 days
1100°C/30 min.

Copper Stabilizer

The reacted wires were coated with a thick Cu layer for mechanical and thermal stability during critical current testing. The Cu layer was electroplated on, and immediately covered with silver solder to prevent oxidation and ensure good electrical contact during subsequent testing.

Critical Current Measurements

Critical current measurements (at 4.2K) were done at the Francis Bitter National Magnet Laboratory, Cambridge, Massachusetts. The samples were placed in a transverse magnetic field, and a standard four-point probe technique was used. A 2 μV/cm criteria was used to define the critical current (I_c). The critical current densities reported are overall : $J_c = I_c$/total cross-sectional area.

Critical Temperature Measurements

Inductive critical temperature measurements were performed for each of the heat treatments listed above. With this method, the sample is placed in a small (a few kG) ripple field and the temperature is slowly ramped from below the T_c where it is diamagnetic (superconducting) to above the T_c where it becomes paramagnetic. An inductive signal is picked up at the transition temperature.

Residual Nb Content Measurements

The area fraction of residual (unreacted) Nb was measured in the 5 wt% Nb-Al powder-powder wire. The wires were reacted at 900°C/30 min. at successive stages of reduction from R=6 to R=10,000. The area fraction of Nb was measured with a digitizer on cross-sectional micrographs. Two techniques were used. The low reduction data points were measured from optical micrographs of anodized wire cross-sections. These were anodized in Pickleshimer's solution for 1 minute at 30 Volts. After anodizing, the Nb regions are bright blue, and the reacted layers are tan and purple.

The anodizing technique is limited to optical resolution. Therefore, for wire reductions above 500, the area fraction of Nb was measured from cross-sectional SEM fracture surfaces. Nb is the only ductile phase remaining in the reacted wire and it appears in the fracture surface as distinct ductile ridges.

Initial (unreacted) Nb layer thickness measurements

The initial Nb layer thickness in the unreacted wires was measured from SEM micrographs of wire cross-sections. The samples were polished and etched for one minute in 10 ml HF, 5 ml HNO_3, and 10 ml HCl. This etchant rapidly dissolves the Al, leaving the Nb regions which were measured. The Nb-5wt%Al powder/powder wire and the Nb-5wt%Al precoated wire were measured at area reductions of 10,000:1. A statistical sampling from (at least 36) randomly selected points were used for the

measurements. The layer thickness at a given point was defined to be the shortest line through the point, which joined two edges of the Nb layer (i.e. the shortest distance between two Nb-Al interfaces).

IV. RESULTS AND DISCUSSION

A. Unreacted wires

The 5wt% Al Nb-Al powder wire was stopped at successive stages of reduction and examined in cross-section. After anodizing, the Nb and Al regions are easily distinguished in color (optical) micrographs as bright blue and silver regions, respectively. Very early in the reduction ,the Nb and Al particles are globular in shape and the Al regions are isolated by large groups of Nb particles. As the drawing is increased, the Nb and Al particles begin to ribbon out, and the Al is better distributed. The beginning of this sequence can be seen in figures 4 a) and b), which are black and white micrographs of anodized samples for R=6 and R=22.

As the drawing is continued, the Nb and Al "layers" begin to intertwine. At the final stages of reduction, the Nb and Al particles have drawn down to form thin convoluted ribbons of Nb and Al. Two SEM micrographs of an unreacted wire cross-section at R=10,000:1 are shown in figure 5. The Al layers have been etched away. As seen in the two micrographs, the Nb and Al layer thicknesses are not uniform. In particular, in some regions the Nb particles have agglomerated to form superlayers much wider than the average value.

Thus the as-drawn wires with their alternating Nb and Al ribbons are an inhomogeneous version of Bormann's multilayers (see Background section). The critical current density is predominantly limited by the extent of A15 (Nb_3Al) formation. If the hypothesis is correct that the A15 reaction only occurs near the initial Nb/Al interface, then the critical current density should depend on the thickness of the layers in the unreacted wires. Higher drawing ratios create more Nb-Al interface per unit cross-section, which is equivalent to forming thinner layers.

As described, the Nb and Al layer thicknesses in a given wire are not single values but distributions about an average. Since it is the Nb particles which are conglomerating

and creating excessively thick regions, the Nb layer thickness was chosen for characterizing the "size" of the unreacted microstructure. Although the Al layer thickness may also play a significant role in the reaction, it appears to be considerably more uniform in a given wire than the Nb layers are, and therefore a less likely candidate for improvement.

Average Nb layer thickness

To study the effect of the average Nb layer thickness on the reaction, a parameter was needed that relates the average layer thickness to wire processing variables. Since the average Nb layer thickness is determined by both the starting powder size and the area reduction ratio (R), a "Nb drawing index" was defined as:

$$t_{Nb} = \text{Nb powder size}/(R)^{1/2}.$$

This equation gives the diameter of a cylinder that would form if a spherical particle were to draw down as a cylinder. This index is particularly useful for comparing the unreacted microstructure of wires in which both the starting powder size and reduction ratios are different. This will be discussed in more detail in the section on reacted wires.

Nb layer thickness distribution

The actual Nb layer thickness distribution was measured in the unreacted wires at R=10,000:1. The thickness at a given point was defined to be the minimum distance between the nearest two Nb-Al interfaces. Figure 6 shows the results, plotted as a histogram. Although there is a peak in the 50-100 nm range, the distribution is quite broad. More than 40% of the measured layers are wider than 200 nm, and only 10% are less than 50 nm.

B. Reacted wires

Average Nb layer thickness

The critical current density (J_c) for a wide range of Nb-Al P/M wires made at this laboratory and by other researchers, was plotted versus the Nb drawing index, t_{Nb} for each wire. As shown in figure 7, the critical current density scales well with this parameter even when the Al content, starting powder sizes, reduction ratios, and heat treatments are varied. The critical current density therefore does appear to depend on the initial Nb layer thickness.

Improvements in J_c can be obtained by increasing the reduction ratio or decreasing the starting powder size. Unfortunately, there are processing limitations to both of these solutions. Use of smaller starting powders has the disadvantage that the total surface oxide is increased and the drawability is degraded (high R cannot be achieved before the wire fails). The highest area reduction ratios currently being used are greater than 1,000,000:1. These high reductions are achieved only in combination with relatively large starting powders, and processing variations at these reductions cause premature wire failure. Therefore, it is also not likely that increases in the critical current density will be obtained by substantially increased reductions alone.

It was necessary to verify that the increase in J_c with decreasing Nb layer thickness is caused by an increase in the extent of the reaction to A15 (Nb_3Al). To do this, the residual (unreacted) Nb content in the reacted wires was measured as a function of the Nb drawing index. The remainder of the wire volume is sigma phase (Nb_2Al) as well as A15 (Nb_3Al). However, it is assumed that the ability to consume Nb is an indication of the relative extent of A15 formation.

The residual Nb content of the 5wt% Al, Nb-Al powder wire was measured at successive reductions from R=6 to R=10,000. As shown in Figure 8, the area fraction of Nb decreases from approximately 70% to approximately 25% when t_{Nb} is decreased from 26 μm to 0.65 μm. Were it not for the distribution problem (excessively thick Nb regions

where Nb particles have conglomerated), this plot should saturate at a t_{Nb} value corresponding to a Nb layer thickness which is thin enough to fully react to A15.

An anodized reacted sample at R=6, and a fractograph at R=7000, are shown in figures 9 and 10 respectively. At area reduction ratios of R=540 and 980, both the anodized (optical) and fracture surface (SEM), methods were used to check for consistency in measuring the residual Nb (see Experimental Procedure). Since Nb is the only ductile phase present in the reacted wires, there is little question that the ductile ridges measured are Nb. Thus the fracture surface method gives a lower limit for the residual Nb. Since the optical and SEM measurements agree, (the optical are slightly *higher*), it appears that the fracture surface is an accurate method of measuring the unreacted Nb content of the wires. Transmission electron microscopy cannot be used for accurate phase content measurements because of preferential thinning during sample preparation.

Nb layer thickness distribution

Although the heat treatment has not been optimized in Bormann's study[23], the results of that study can be used as a rough indication of the maximum layer thicknesses than can fully react to A15 (Nb_3Al) in the wires. The Nb layer thickness was approximately 50 nm in the thinner multilayered samples (which fully reacted to stoichiometric A15) and 100 nm in the thicker samples (which contained sigma phase and residual Nb). Therefore, the initial layer thicknesses measured in the wires predict that approximately 40% of the wire volume should contain sigma phase and residual Nb after reaction .

The presence of sigma phase indicates that at least some of the A15 (Nb_3Al) in the wires is off-stoichiometric. In addition to the increased volume fraction of superconducting phase that could be obtained if the wire were able to fully react to A15 (Nb_3Al), an improved distribution, with thin enough layers, would allow the formation of higher quality A15, and therefore higher critical current densities. This is probably the reason that

some of the non-equilibrium techniques have generated Nb_3Al samples with J_c values more than 10 times that of the best powder wires [18]. The volume fraction alone would result in at most a 2-3 fold increase in J_c.

Optimum Aluminum Content

Researchers in the past have reported different values for the optimum Al content for Nb-Al powder wires (the Al content which gives the highest J_c) [1,3,4,5]. The J_c versus Al content data for two sets of wires made at another laboratory are plotted together in figure 11. Both the starting powder sizes and the reduction ratios are different in each set; therefore the Nb drawing index (t_{Nb}) has been labeled as an indication of the average layer thicknesses. The optimum Al content appears to depend on the average Nb layer thickness.

The optimum Al content can also be understood in terms of the total amount of Nb/Al interface (i.e. the thickness of the Nb and Al layers). The peak occurs when, on the average, the available Nb surfaces are saturated with Al. As the Al content is increased from below the peak value, adding more Al creates more Nb/Al interface (breaks up the Nb-Nb interfaces) and more Nb_3Al can be formed during reaction. Since the Al content is cited as a percentage, increasing the Al content is equivalent to removing Nb. Increases above the peak value are decreasing the total amount of Nb/Al interface (perhaps causing Al/Al interfaces to exist). When the average Nb layer thickness (t_{Nb}) is decreased, the peak shifts to higher Al content because more Nb surface is available, and more Al can be accommodated before the saturation point. As expected, this gives a higher J_c.

C. Precoated powder wires

Even when the average Nb layer thickness is sufficiently small, the local agglomeration of Nb particles creates excessively thick layers which cause the formation of off-stoichiometric A15 (Nb_3Al) and sigma phase (Nb_2Al). There is evidence that when

the distribution is improved (that is, when more of the Nb/Nb interfaces are broken up by Al layers), the J_c improves. As seen by Foner et. al.[1] increases in the critical current can be obtained by decreasing the initial Al powder size. However, the best of these wires still have substantial amounts of sigma present, as well as unreacted Nb, which indicates that the distribution can be further improved[16]. Additionally, as mentioned, the highest reduction ratios have not been obtained in combination with the smallest starting powders. In the ideal situation, every Nb particle would be surrounded by an Al layer.

In an attempt to improve the distribution, a set of wires were made in which the loose Nb powders were precoated with Al by evaporation. This method of wire fabrication by precoating proved feasible. The wire drew easily to $R=10^4$ at which point the drawing was stopped because the wire diameter had become prohibitively small. As shown in Fig.12, the critical current density of the precoated wire was as good, if not slightly better, than that of the similarly processed reference wire. However, substantial increases in the critical current density were not observed.

To determine whether the precoating process had improved the distribution, the actual Nb layer thickness distribution was measured, as for the powder-powder reference wire. The results, shown in figure 13, indicate that the distribution has been improved in the precoated wire. In the powder/powder wire, more than 40% of the measured layers are wider than 200nm. In the precoated wire, the distribution is more sharply peaked, and less than 20% of the measurements are greater than 200 nm.

However, although the distribution has been improved in the precoated wires, in both sets of wires only 35-40% of the layers are less than 100 nm wide. Only these layers are able to fully react to A15 (Nb_3Al). The improved distribution of the precoated wires would need to be shifted to smaller values for an improvement in J_c to occur. This seems to explain why the critical current densities are similar for the precoated and powder-powder wires, in spite of an improved distribution.

This precoating method, combined with a higher reduction to decrease the average value, should yield a substantially improved wire. Therefore, to further test this method of wire fabrication as a method of increasing the current carrying capacity, higher reductions using this precoating process are necessary. In addition, a new multilayer study is being performed, using the relevant (optimized) heat treatments and including transmission electron microscopy of the reacted layers.

V. CONCLUSIONS

The maximum critical current density of powder-processed Nb-Al superconductors is determined by the limited extent of the reaction that forms the superconducting A15 phase (Nb_3Al), and the quality (stoichiometry) of the A15 formed. The remainder of the reacted wire consists of sigma phase (Nb_2Al) and residual niobium. The reaction (to A15) during optimized heat treatments appears to occur only over a thin region near the initial Nb-Al interface. The presence of sigma phase causes off-stoichiometric A15 to form. Therefore both the quality of the A15 and the extent of formation depend on the size of the Nb and Al regions in the unreacted wires (i.e. the amount of Nb-Al interface per unit cross-sectional area).

The powder particles in the unreacted wires form thin sandwiched layers of Nb and Al. These layers are convoluted in shape, and in some regions the agglomeration of Nb particles causes excessively thick layers to exist. The average Nb layer thickness was characterized by a "drawing index": t_{Nb}=initial Nb powder size/(area reduction)$^{1/2}$. The critical current density was found to scale well with this process parameter, indicating that the initial (unreacted) Nb layer size plays a dominant role in the extent of the reaction. The increase in the extent of the reaction with decreasing (average) Nb layer thickness was verified by measurement of the residual (unreacted) Nb content in the reacted wires, which decreased with the Nb layer thickness.

A recent study of deposited Nb-Al multilayers made by sputter deposition indicates that Nb layers approximately 50 nm thick should fully react (to Nb_3Al), and layers in excess of 100 nm will form off- stoichiometric Nb_3Al, sigma phase, and residual Nb. The layer thickness in the unreacted wire is inhomogeneous. Measurements of the initial Nb layer thickness (at $R=10^4$ and t_{Nb}=650 nm) showed a broad distribution from 50-750 nm, with a slight peak in the 100-200 nm range.

To avoid the agglomeration of Nb particles which causes excessively thick regions, a set of wires were made in which the loose Nb powders were precoated with

Al. This resulted in a slight improvement in critical current density. Measurement of the initial Nb layer thickness showed that although the distribution was significantly improved, the average layer thickness was still too large to expect full reaction. Therefore, higher reductions of this wire are currently under investigation.

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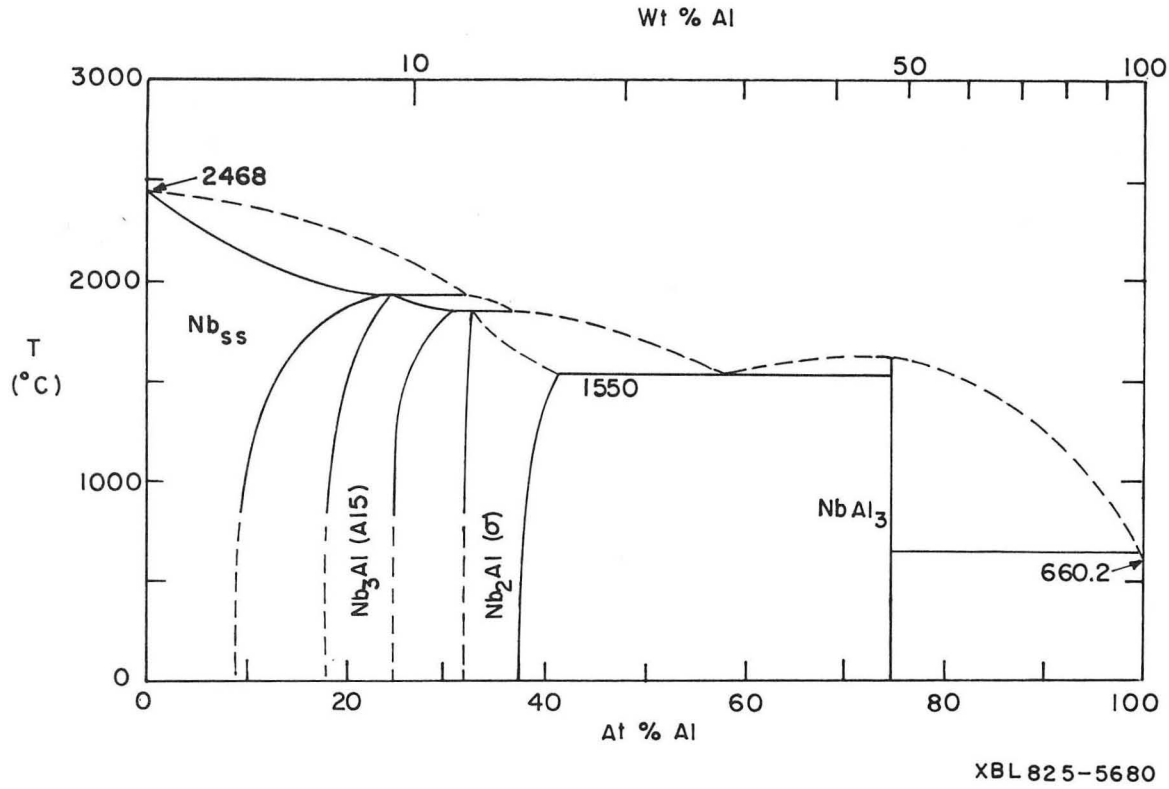

Figure 1. The Nb-Al phase diagram.

Figure 2. TEM micrograph of a longitudinal section of the Nb-5wt% Al powder wire after reaction at 1100°C/20 minutes. The clear equiaxed grains are A15, and the thick small-grained region in the center is sigma phase. XBB 874-3452

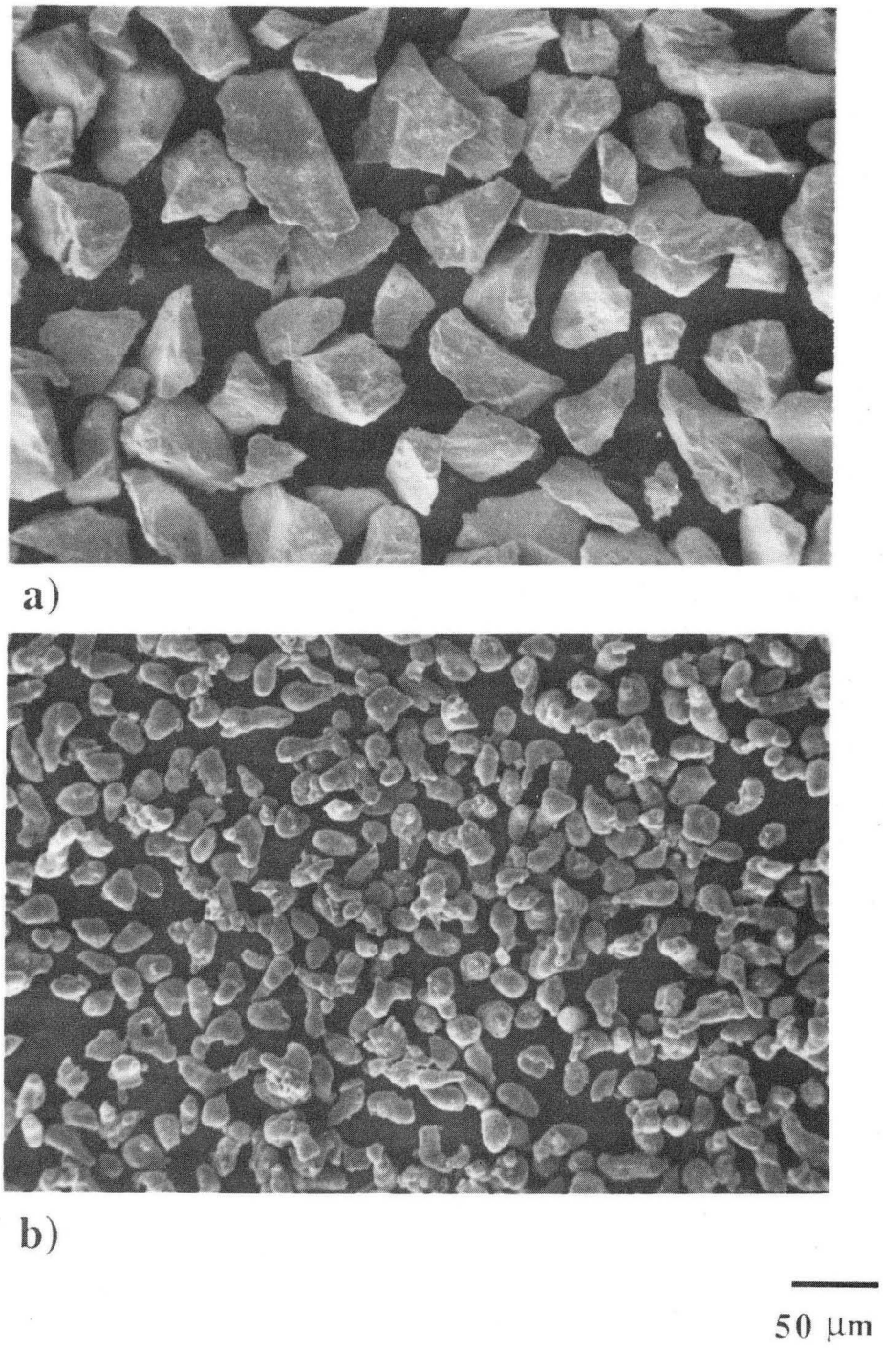

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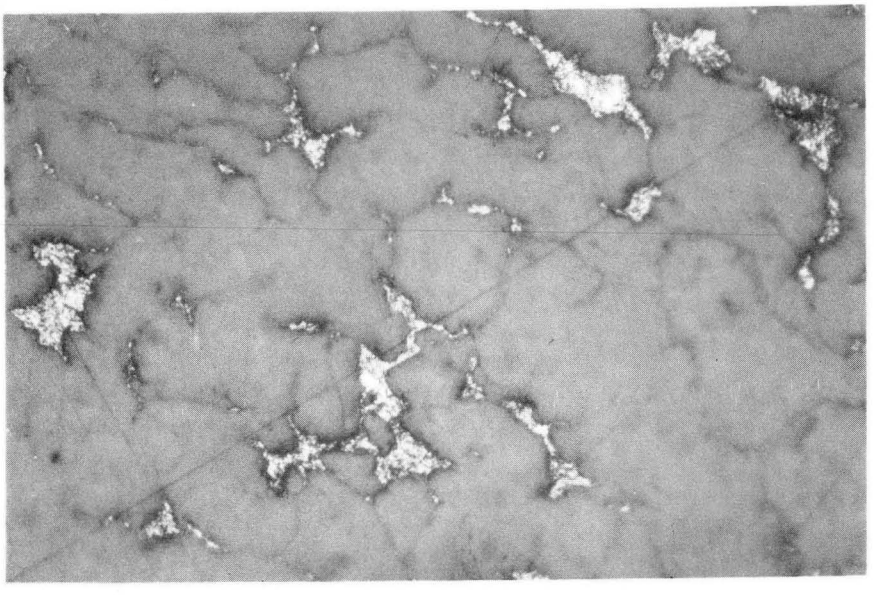
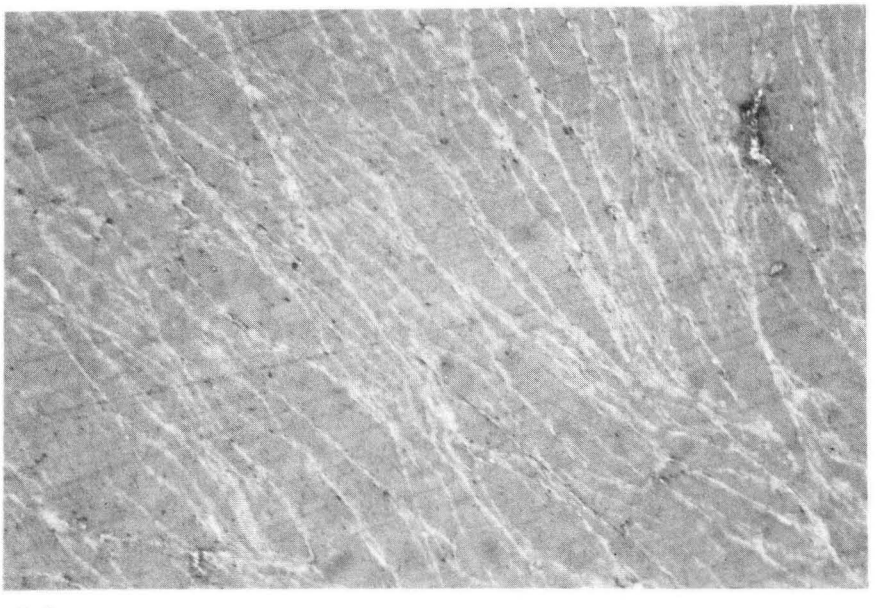
Figure 3. a) Niobium powders and b) Aluminum powders used in the powder wires.

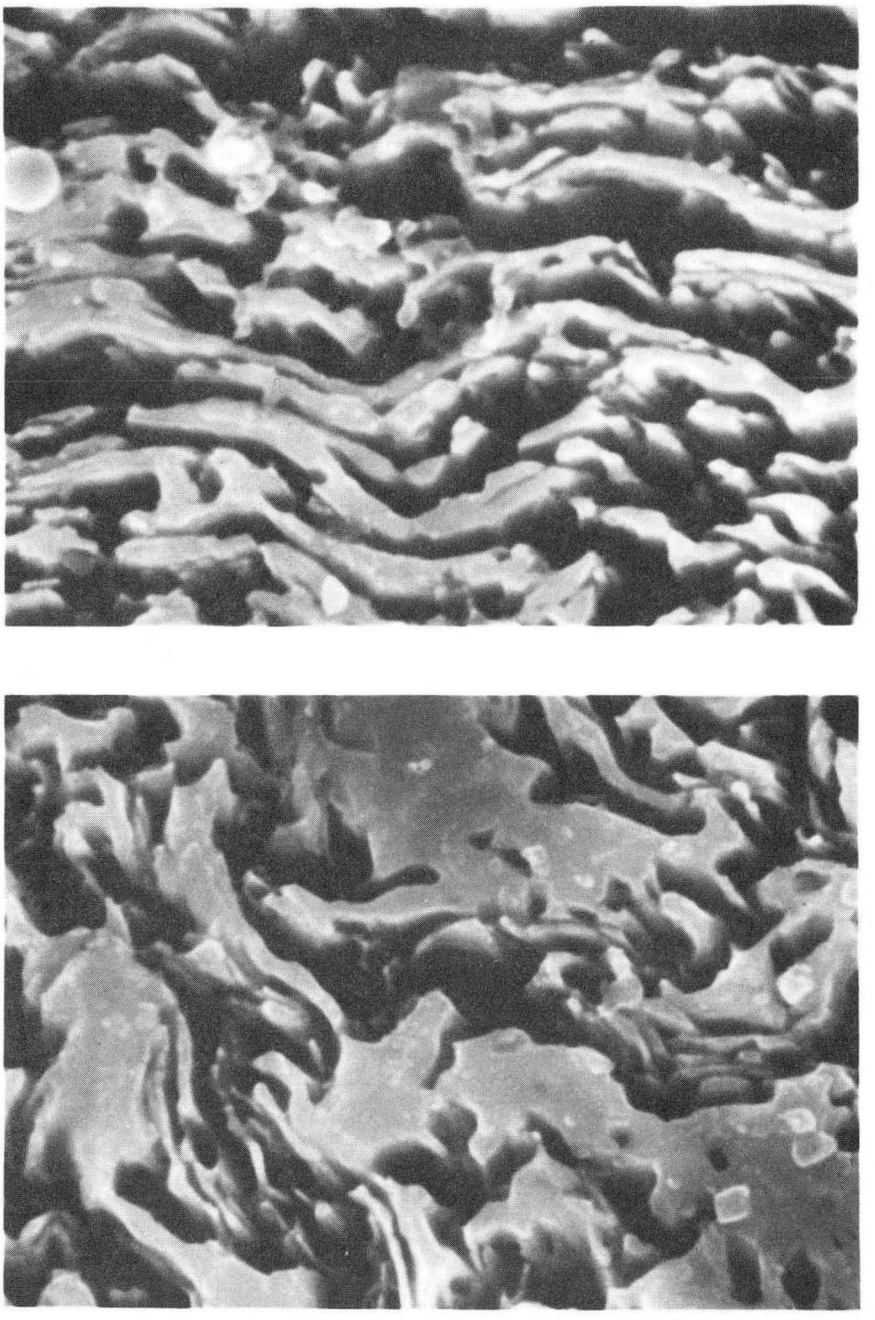


a)



b)

Figure 4. Anodized unreacted wire cross-sections early in the drawing at a) R=6 and b) R=22. XBB 874-3455



300 nm

Figure 5. Unreacted wire cross-section at R= 10,000. The aluminum layers have been etched away.

XBB 874-3456

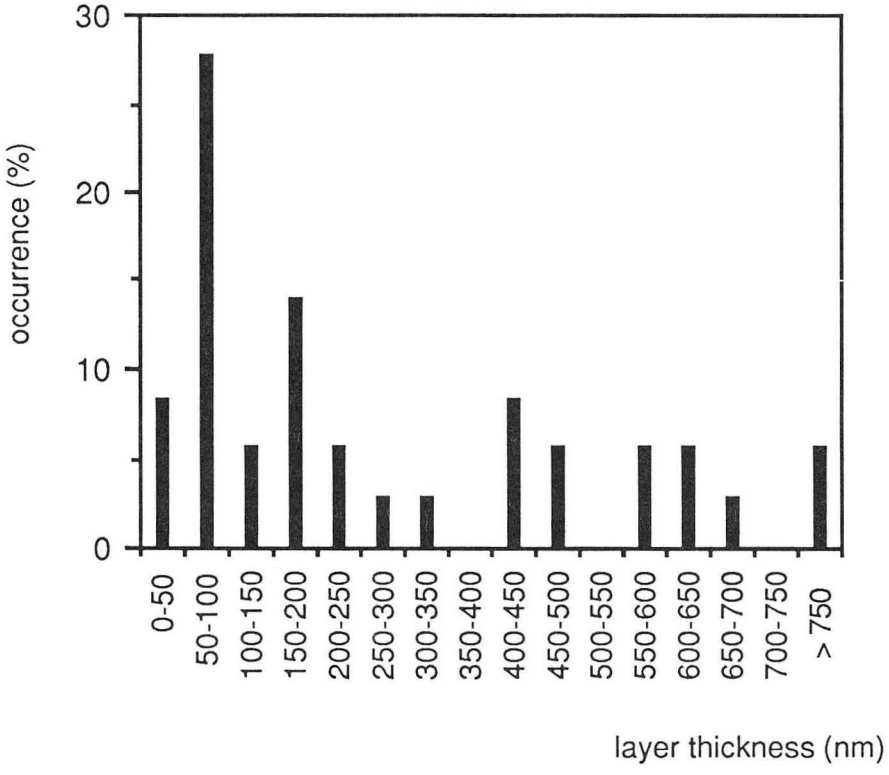


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Figure 6. Initial (unreacted) Nb layer thickness distribution for the Nb (65 μm)-5 wt% Al (20 μm) powder wire at R=10,000.

No.	w% Al	Nb(μm)	Al(μm)	R	Heat treatment
1 [a]	3	40	9	1400	800 °C/16hr.
2 [b]	4	65	20	10000	900 °C/20min.+ 750 °C/2d.
3,4,5, 6,7 [b]	5	54	20	6300-17700	900 °C/20min.
8,9 [a]	6	150	9	60000-80000	900 °C/30min.+ 750 °C/3d.
10,11, 12,13 [a]	8	150	19	25000-80000	900 °C/1-3hr.+ 800 °C/20-50hr.
14 [a]	10	150	9	60000	900 °C/1hr.

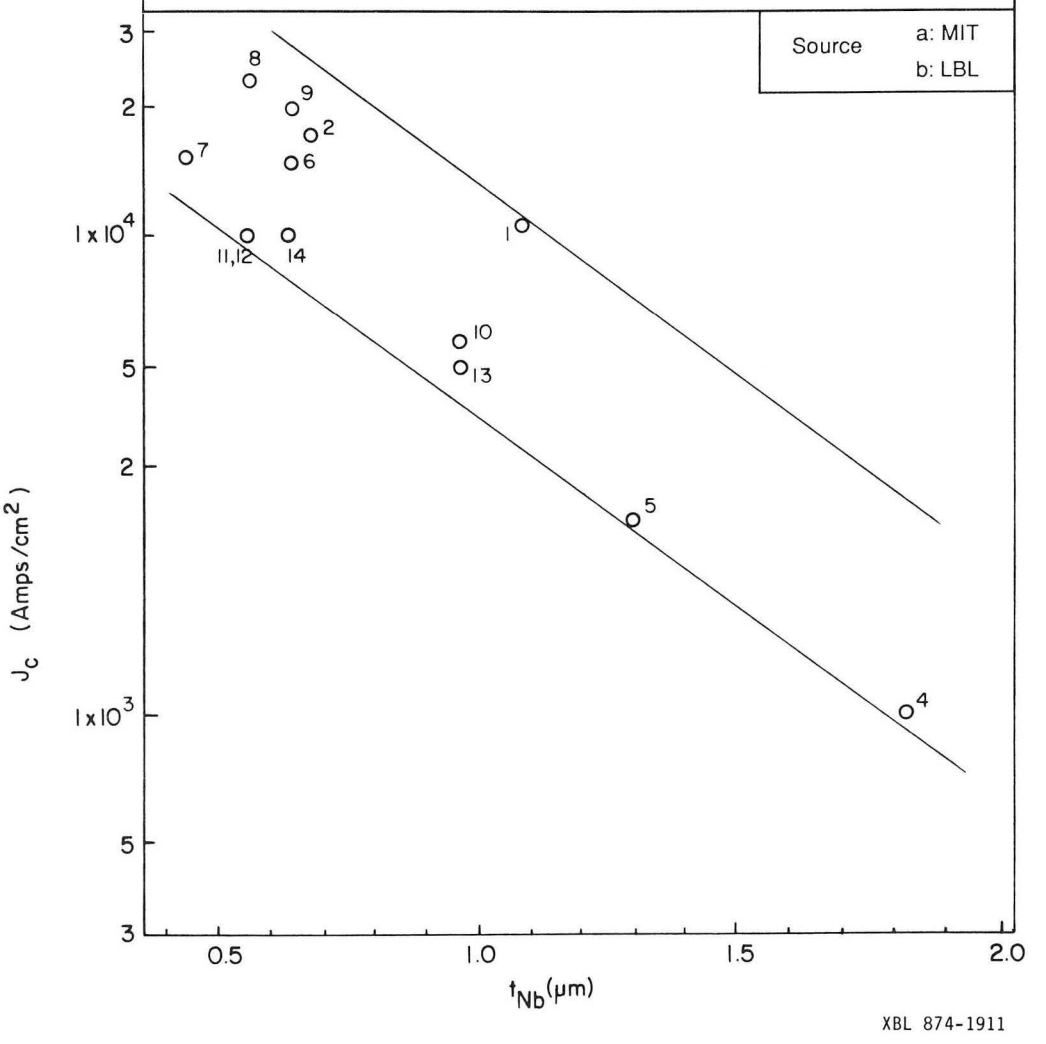


Figure 7. Overall critical current density at 14T vs the Nb "drawing index" defined as t_{Nb}=Nb powder size/$(R)^{1/2}$.

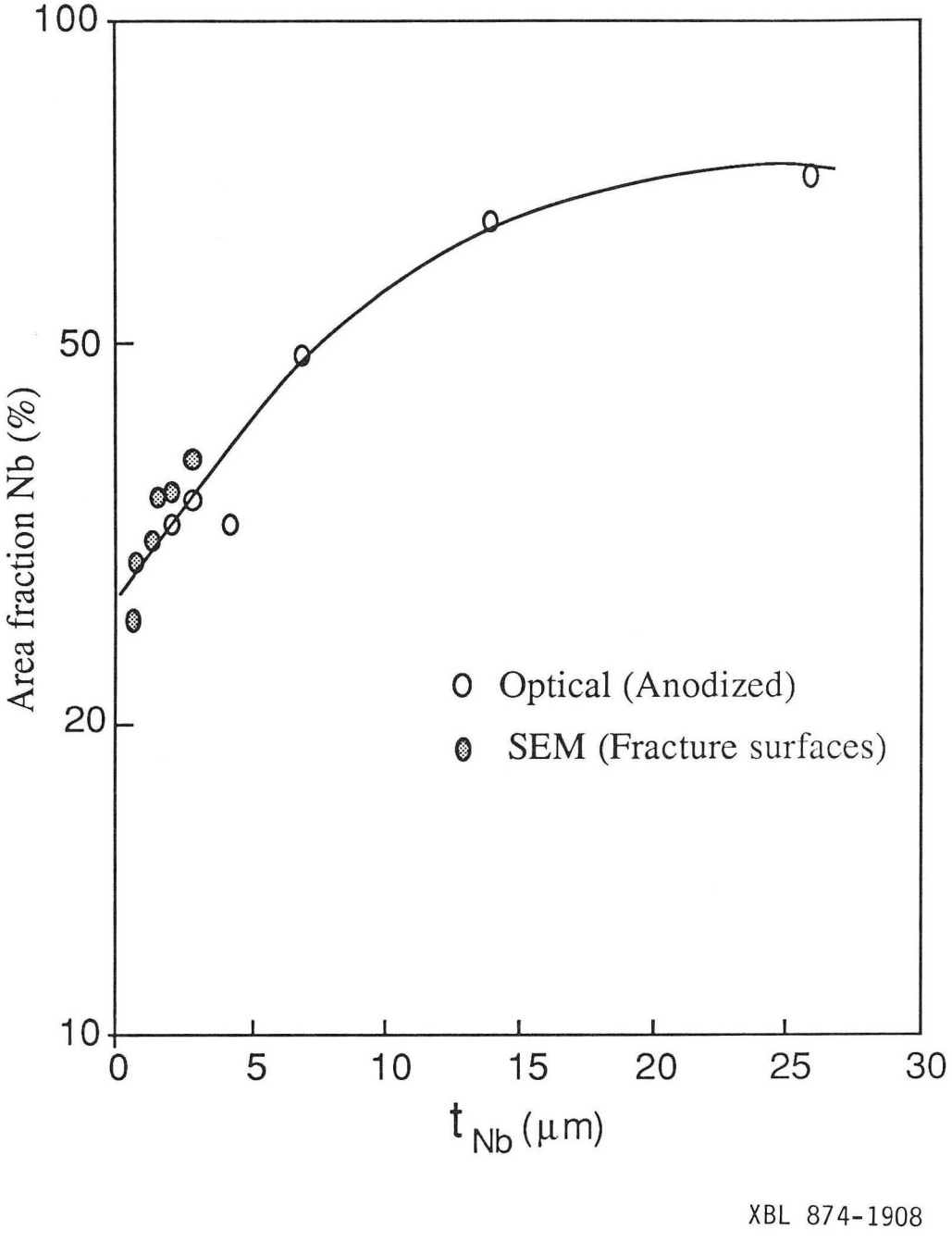
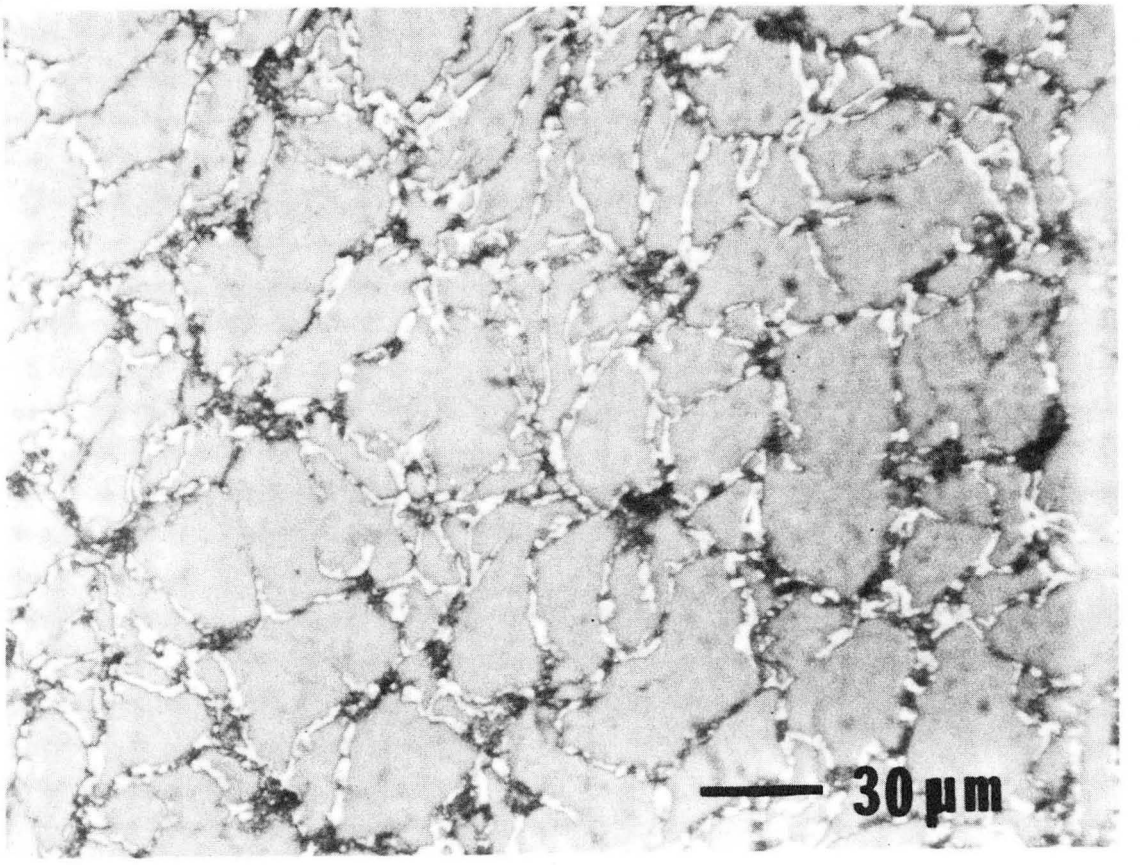
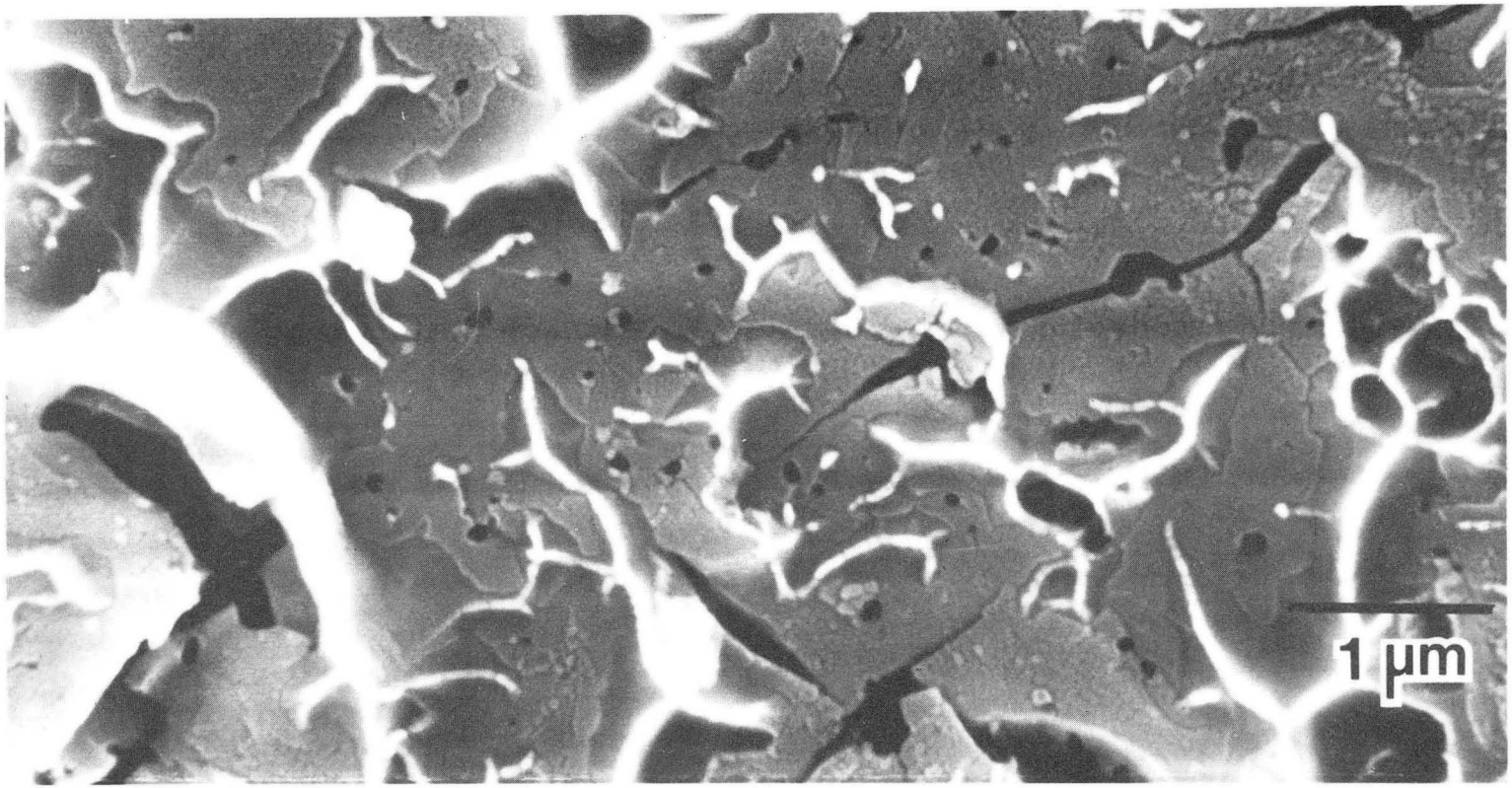


Figure 8. Area fraction of residual Nb after reaction at 900°C/30 min. vs t_{Nb} for a Nb(65 μm)-5 wt%Al (20 μm) powder wire.



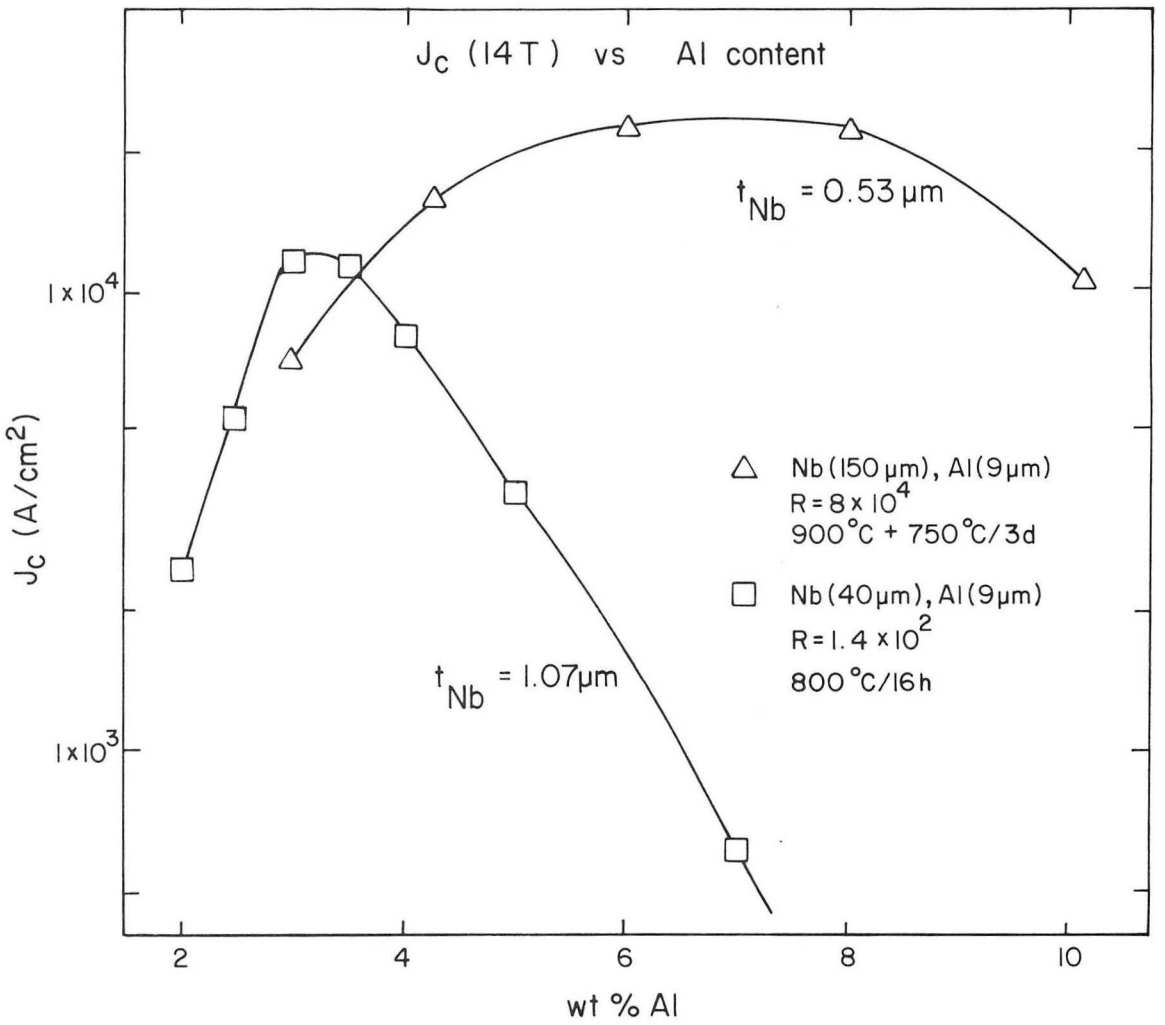
CBB 861-610

Figure 9. Anodized (optical) micrograph of a reacted wire cross section (Nb-5wt%Al powder wire, at R=6, reacted at 900 °C/30 minutes). The large, clear regions are residual (unreacted) Nb.



XBB 869-7718

Figure 10. SEM fractograph of a reacted wire cross-section (Nb-5wt% Al powder wire, at R=7000, reacted at 900°C/30 minutes). The raised ridges are residual (unreacted) Nb.



XBL 874-1912

Figure 11. Overall critical current density at 14T vs aluminum content for two sets of Nb-Al powder wires. Adapted from references 1 and 3.

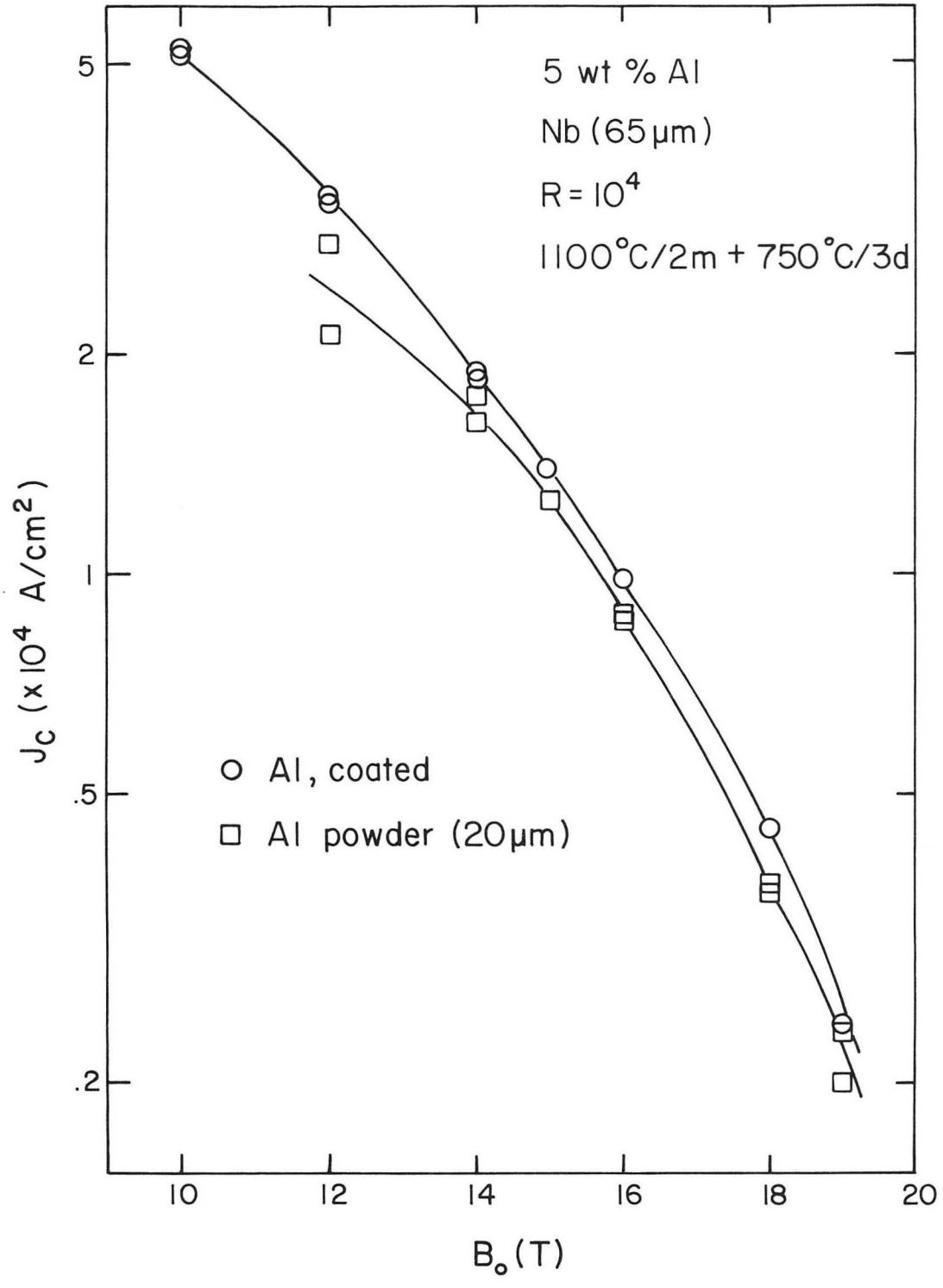
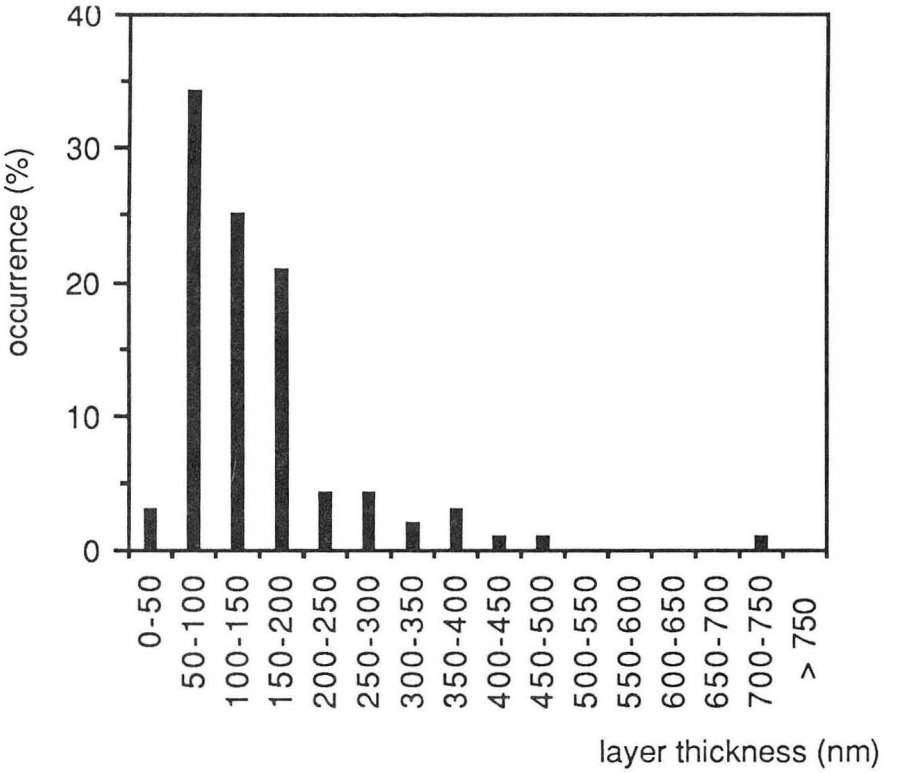


Figure 12. Overall critical current density versus applied magnetic field for the Nb-5wt% Al precoated and reference wires.



XBL 874-1910

Figure 13. Initial (unreacted) Nb layer thickness distribution for the Nb(65 μm)-5 wt%Al precoated powder wire.

Appendix A

BULK NB-AL DIFFUSION COUPLES

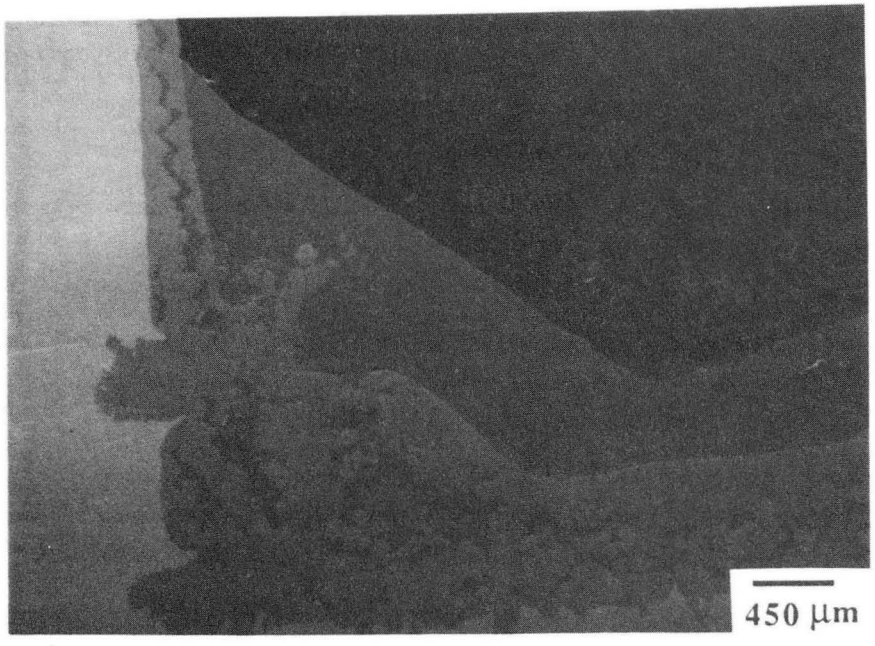
A set of bulk diffusion couples were made to study the reaction of niobium and aluminum at temperatures near 900°C when the Nb and Al layer thicknesses are essentially infinite. This was intended to study the reaction at the interface, and possibly determine the maximum thickness of A15 that a single interface could produce.

In one set of samples, pieces of Nb (99.99%) were machined into "boats", the inside of which were polished. An 1/8" thick piece of Al (99.999%) was fitted inside each boat, and the assemblies were sealed in evacuated quartz tubes backfilled with argon, and reacted at 900°C for 30 min. to 5 days. In all cases, the only phase present (other than unreacted Nb and Al) was $NbAl_3$. This was verified by SEM with X-ray spectroscopy (KEVEX) which showed a 75 at% Al composition, and by anodizing the samples with Pickelshimer's solution which showed a single reacted phase. Figure A-1 a) and b) show one of these samples. It appears that $NbAl_3$ particles are forming at the Nb-Al interface, breaking off, and being carried away by the liquid Al. These samples, even when put back in the furnace, and the remaining Al allowed to melt off, showed no A15 (Nb_3Al) or sigma (Nb_2Al) formation after heat treating at 900°C for 2 weeks. In contrast, the Nb-Al powder wires have substantial amounts of A15 formed after heat treatments of 900°C/30 min.

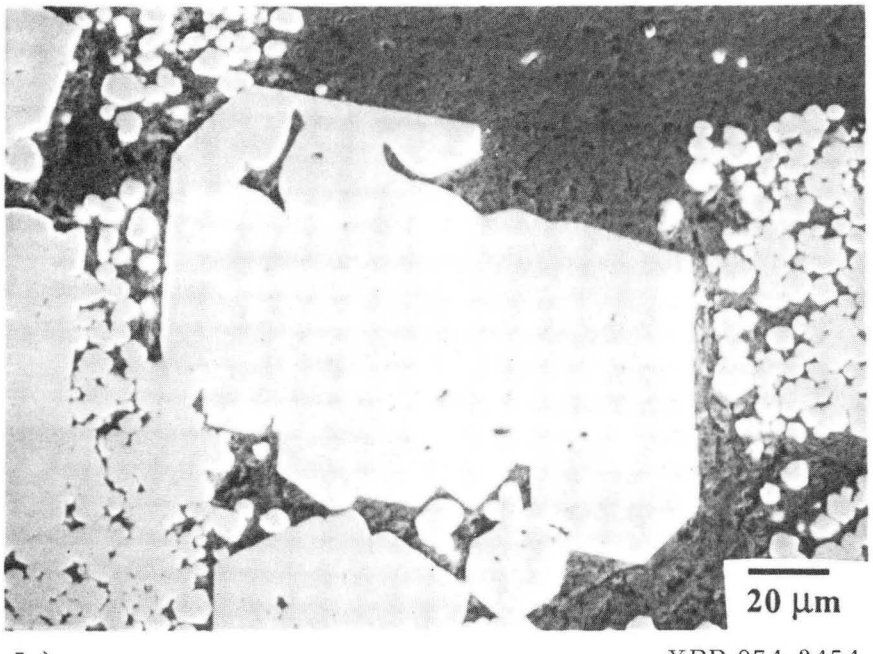
A series of diffusion couples were then made to determine if the deformation of the Nb in the powder wires might be an important factor in the reaction at the Nb-Al interface. A one-inch thick Nb plate (99.99%) was cold rolled to 75%, 50%, 25%, 10%, and 2% of its original thickness. Pieces were then cut and polished, Al (99.999%) was placed on top, the pieces sealed in quartz tubes, and heat treated at 900°C. Again, after heat treatments ranging from 20 minutes to 5 days, the only phase seen was $NbAl_3$.

Since no higher resolution (TEM) studies have been done on these samples, it is possible that a very thin layer of A15 (Nb_3Al) or sigma (Nb_2Al) is present near the initial Nb-Al interface. However, if it is true that no A15 (Nb_3Al) is present, then the reaction at

the initial Nb-Al interface depends on the thickness of the Nb and/or Al away from the interface. This is inconsistent with current theories on the path of the reaction. Therefore, future work should include separately addressing the dependence of the reaction on the Nb and Al thickness.



a)



b)

XBB 874-3454

Figure A-1. Bulk Nb-Al diffusion couple. a) On the left and bottom is unreacted Nb, bordered by the $NbAl_3$ layer, above which is Al (the upper right is mounting material). b) $NbAl_3$ particles surrounded by Al.

Appendix B

TERNARY ADDITIONS OF GERMANIUM

Introduction

An alternative solution for increasing the critical current density by increasing the extent of A15 (Nb_3Al) formation in the wires is the use of ternary additions which stabilize the A15 reaction. In the Nb-Al system, the A15 phase forms in competition with the more stable sigma phase (Nb_2Al). In addition to decreasing the amount of A15, the presence of the sigma phase causes the A15 (Nb_3Al) that is formed to be off-stoichiometric, and thereby degrades its quality[B1]. The extent of formation and the quality of the superconducting phase can therefore be enhanced by finding a method to suppress the formation of the sigma phase. The ternary addition, incorporated in the A15 (Nb_3Al) phase, must also not degrade the superconducting properties of the A15 (i.e. it must form a high T_c high H_{C2} superconductor).

A survey of existing literature indicates that Ge is a first choice candidate, followed by Si or Ga. The ternary A15 compound, $Nb_3Al_xGe_{1-x}$ ($x<1$), is capable of carrying high current densities, has an upper critical field of about 41T, and a critical temperature of 20.7K. When added to the Nb-Al system at the right composition, Ge is also expected to suppress the formation of sigma (Nb_2Al) phase. There are of course, some problems involved in obtaining this higher performance ternary compound, the most prohibitive of which is the limited deformability of Ge, which has thus far prevented it from being incorporated into a drawn wire. The existing information on the Nb-Al-Ge ternary system has come from small-scale lab samples and non-equilibrium techniques such as those discussed in the Background section.

The Nb-Al-Ge ternary phase diagram[B2] is shown in fig B-1. One explanation for the ability of Ge additions to suppress formation of the sigma phase is as follows[B1,B3]. In the A15 (A_3B) crystal structure , all B atoms have A atoms as nearest neighbors. In the sigma structure, some of the B atoms have B atom nearest neighbors. If B atoms

(germanium in this case) are substituted for another type of B atom (aluminum), the two types of B atoms are forced to interact chemically in the sigma crystal structure, but not in the A15 crystal structure. Since Al and Ge do not mix well at all, Ge additions might be expected to enhance formation of the A15 superconducting phase by destabilizing the competing sigma phase (Nb_2Al).

Techniques for producing Nb-Al-Ge alloys included: rapid quenching from a liquid[B4-B7], sputter deposition[B8-B10], arc-melting of powder compacts[B11-B-13], and liquid infiltrated porous Nb rods[B14,B15]. These methods will not be comprehensively reviewed here, but they have produced high T_c, high H_{C2} compounds, some of which also have very high critical current densities. The optimum properties have been obtained at an A15 composition of approximately $Nb_3Al_{.75}Ge_{.25}$. As part of the current work, several methods were used to incorporate Ge into a drawn Nb-Al powder wire. This section documents these efforts. In each case, it was attempted to hold the Al to Ge atomic ratio at approximately 3:1, and maintain the Nb to (Al + Ge) atomic ratio equivalent to the optimum Al content in the Nb-Al powder wires (about 18 at% Al, depending on the starting powder size and reduction ratio).

Ge added to the Al as an Al-Ge eutectic

An Al-Ge alloy (5 lbs) at the eutectic composition (54 wt% Ge) was cast in a copper cooled mold. An Al-Ge powder was then made by filing powder from the slab. The resulting powder was mixed with Nb powders which had been ground as a hydride in a ball mille, sieved, and then dehydrided. The powder mix was compacted in a Monel tube, then swaged and drawn.

The resulting wire failed at very low reductions. SEM with X-ray spectroscopy (KEVEX) showed that at the failed regions of the wire contained large Ge-rich particles which had torn through the adjoining material during drawing, and caused the wire to fail. These were presumed to be regions of Ge-rich phase present in the original eutectic

microstructure of the Al-Ge slab. A more ductile Al-Ge powder could possibly be produced by gas atomization of Nb-Ge alloys from a melt. A source for such powders has been contacted, and this alternative is currently being investigated.

Ge added as a Nb-Ge alloy

The equilibrium solubility of Ge in Nb is about 2 wt% at 1000°C. In an effort to obtain a ductile Nb-Ge powder for use in the wires, a Nb-2 wt% Ge powder was made. Nb and Ge (99.99%) powders were mixed at 2 wt% Ge, compacted, and sintered under vacuum. The compact was then arc melted, and homogenized at 1800°C for 24 hours. The alloy was then made into a hydride, ground, sieved, and dehydrided. The powder was mixed with 6 wt% Al, compacted in a Monel sleeve, swaged and drawn.

Again, the drawability of the wire was severely limited. The probable cause of this failure to form a ductile wire was attributed to the necessity of using a relatively slow furnace cool for the Nb-Ge powder after the dehydride process. The slow cool allowed the formation of brittle Nb-Ge intermetallics. The furnace cool was chosen rather than expose the powders to air while at high temperatures, which might cause oxidation and subsequent embrittlement. Adding the Ge in this way might be successful (in yielding a ductile powder) if the powders were instead rapidly cooled after the dehydride to quench in the dissolved Ge. This method however, was not further pursued.

Addition as fine dispersion of elemental Ge

A mixture of Nb-5wt%Al powders were prepared as for the standard Nb-Al powder wires. Elemental Ge (99.99% purity) was ground in a W-C ball mille for approximately two weeks, producing a fine (submicron) powder which was used to coat the Nb-Al powder mix. As it was not possible to grind the Ge in an inert environment with this equipment, no effort was made to prevent the Ge powder from oxidizing.

The resulting dispersion of Ge (4.3 at%) onto the mixed powders appeared uniformly distributed in SEM. However, the wire failed during subsequent drawing at a maximum reduction ratio of R=200. The wire "filaments" did not adhere well, and the failed wire ends had a frayed appearance, rather than the cup and cone fracture surface that more typically occurs during wire drawing.

Ge added by precoated Nb powders

A Nb-Al-Ge wire was made by precoating the loose Nb powders by evaporation. Nb powders were processed as for the Nb-Al powder wires. The loose powders were then spread in a 10" (25 cm) diameter tray and coated first with Ge, then with Al. The resulting powder (50 gm Nb, 1.1 gm Ge, and 2.3 gm Al) was placed in a Monel tube, and swaged and drawn.

The wire drew down to an area reduction of R=2500 before failure (a cup and cone fracture surface was seen). Subsequent critical current testing on this wire (and a precoated Nb-Al reference wire tested at the same R) showed that gross inhomogeneities existed along the length of the wire. This was attributed to an inhomogeneous distribution of Ge in the wire, perhaps in the as-coated powders. It is possible that modifications of this process, with a method to ensure a thin, even coating of Ge on the powders, would be successful in producing a ductile wire to adequately test the effect of Ge additions.

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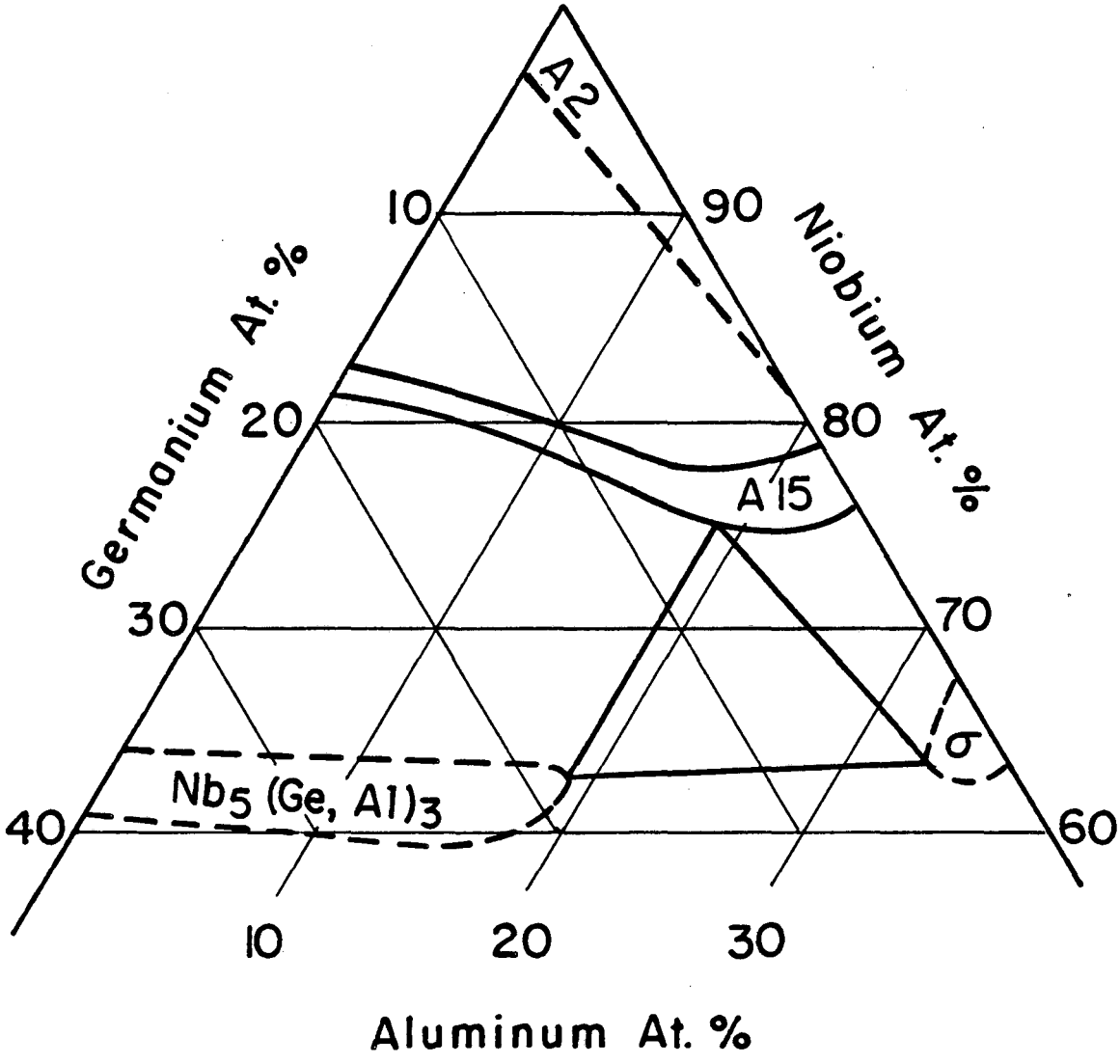

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Figure B-1. The Nb-Al-Ge ternary phase diagram at 1840 °C[31].

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