DESIGN PARAMETERS FOR PROCESSING FLEXIBLE
Nb₃Al HIGH FIELD SUPERCONDUCTING TAPES AND WIRES

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DESIGN PARAMETERS FOR PROCESSING FLEXIBLE
 Nb_3Al HIGH FIELD SUPERCONDUCTING TAPES AND WIRES *

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ABSTRACT

A process has been developed to fabricate Nb_3Al composite wires at a temperature below 1000°C . This process consists of a solution heat treatment which forms a metastable solid solution upon quenching. The solid solution transforms to the A-15 phase by subsequent low temperature aging. The onset temperature of superconductivity of the resulting material, as measured inductively, was $17.6 \pm 0.5^\circ\text{K}$. This is 2°K higher than has been previously reported for Nb_3Al formed below 1000°C . Using this process, large Nb_3Al layers are formed in a ductile Nb matrix. Extensive twinning has been observed to occur in the metastable solid solution subjected to plastic deformation.

The results of this study can provide the basis for the development of a process for producing a fully stabilized Nb_3Al conductor with high values of T_c and J_c .

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I. INTRODUCTION

With dwindling world wide reserves of fossil fuel and increasing demand for power much effort is being expended to find new ways to generate and conserve energy. Superconductors are critical to the development of controlled thermonuclear fusion reactors, and can be used to more efficiently convert fossil fuels into energy by magnetohydrodynamics. At the same time superconductors have the potential for loss-free transmission of electricity, and for the development of magnetically levitated trains. These are but a few of the possible uses of superconductors. The most important property of a superconductor is its ability to develop large magnetic fields with minimal power losses when wound into coils. Superconductors can be divided into two major classes; low field ductile solid solutions and high field intermetallic compounds. There are three critical parameters which govern the transition from the superconducting to the normal states: temperature, current density and applied magnetic field. The most widely used material at present is the ductile NbTi which remains superconducting only in weak magnetic fields and at a very low temperature (10°K), but is easily processed by conventional techniques. The best superconductors are the extremely brittle A-15 compounds (see Fig. 1) which can develop high magnetic fields at temperatures above 20°K , but which demand special fabrication methods. A critical temperature of 20°K not only will decrease the refrigeration cost, but also raises the possibility of using liquid H_2 rather than liquid He to cool the superconductor. This will also drastically reduce the overall cost. For this reason intensive research is being

conducted to develop to a commercial level many of the high field superconducting materials. Only the systems based on V_3Ga and Nb_3Sn have been advanced to the point of being available in a functional form, while several superior materials have gone essentially undeveloped.

This report is concerned with the study and development of a process to fabricate one of the best known superconductors, Nb_3Al . The objectives are discussed along with a short historical background in Sections II and III. Design parameters were studied on bulk samples and the results are presented in Section IV. Using the knowledge gained in these feasibility studies, a process was developed to fabricate functional shaped superconductors and their characteristics are discussed in Section V. The superconducting properties were determined and compared in Section VI with those of the same compound prepared by other reported methods. Conclusions and projections for further studies are made in the final sections.

II. HISTORICAL NOTE

Since the discovery of superconductivity in 1911 by Kammerlingh Onnes,¹ the interest in superconductivity was limited until 1954 when Hardy and Hulm² reported a transition temperature of 17.1°K for the A-15 compound V_3Si . The same year Matthias et al.³ discovered the intermetallic compound Nb_3Sn with a $T_c = 18.05^\circ K$.

In 1961 Kunzler et al.⁴ observed that superconductivity persisted in Nb_3Sn when subjected to high current densities (10^5 A/cm²) and to high magnetic fields (8.8 T). This discovery opened new areas of applications for superconductors such as high energy physics where high field magnets are needed.

The earliest commercial superconductors were ductile alloys of niobium and titanium which were easily fabricated. The processing of Nb_3Sn on the other hand demanded new techniques in order to overcome its extreme brittleness. The first usable Nb_3Sn wire was produced by Kunzler⁴ who packed elemental powders of Nb and Sn into a Nb tube, mechanically reduced the size and finally reacted the powders to form Nb_3Sn . This wire could be easily wound into a coil prior to reacting, but after the brittle Nb_3Sn had been formed no further mechanical deformation was possible. This inherent pitfall of the "wind and react" technique has been overcome by present day methods. Very fine filaments of the superconducting phase are formed by solid state diffusion processes in a ductile matrix close to the neutral axis of bending. This allows significant coiling of the conductor without substantial degradation of the superconducting properties.

Along with solid state diffusion processes, new methods such as chemical vapor deposition and rf sputtering have shown promise in obtaining good superconducting properties in thin films in many systems, such as Nb_3Ga , Nb_3Ge and $\text{Nb}_3\text{Al}_{0.75}\text{Ge}_{0.25}$.⁵⁻⁷ Another method which has been used with limited success is the processing of metastable solid solutions. In both the V-Ga⁸ and Nb-Sn⁹ systems bulk metastable solid solutions can be prepared and the ductility of these samples is such that the material can be deformed. This, however, is of little practical value since alternative methods have been developed for both compounds which result in superior superconductors.

In the Nb-Al system, however, there is no process to date which optimizes the potential of this compound. The ultimate result of the present work defines the parameters of a process which is a sequence of a solution reaction, rapid quench, and a low temperature aging treatment to convert the metastable solid solution to the A-15 phase. Using this technique, superconducting Nb_3Al was formed in a manner more likely to produce optimized properties.

III. OBJECTIVES

This work was undertaken with the hope that it would lead to the development of a usable superconductor based on the niobium-aluminum system. As a result of the inherent brittleness of the superconducting intermetallic compound, Nb_3Al , a new approach was attempted. This method takes advantage of the increasing solubility of Al in Nb with increasing temperature (see Fig. 2). At room temperature Nb can dissolve only 8 at.% Al, whereas the maximum solid solubility of Al is about 23 at.% at 1950°C. It was reasoned that a sample heated into the high temperature solid solution region of the phase diagram could be quenched rapidly enough to retain the solid solution and prevent transformation to the stable A-15 phase. Once quenched, the solid solution might be ductile enough to withstand significant plastic deformation. In this way it could be processed by traditional techniques. Another important feature would be that having the material in a metastable state, it could be transformed to the superconducting phase by a low temperature aging treatment. It is desirable, from the standpoint of the superconducting properties, T_c and J_c , that the A-15 phase be formed at a temperature below 1000°C. The critical temperature of Nb_3Al is strongly dependent upon the degree of atomic order of the Nb and Al atoms in the A-15 lattice.^{10,11} For this reason, material formed by high temperature diffusion processes is often subjected to long low temperature anneals.^{12,13} This restores much of the atomic order which had been destroyed by the high temperature treatment. The critical current carrying capacity is dependent upon the amount and efficiency of the magnetic flux pinning centers present in the superconducting phase.¹⁴ Flux pinning centers can be oxides, vacancies

or any other type of discontinuity in the structure. Grain boundaries are very effective pinning centers and the smaller the grain size the better is the pinning effect. The grain size of the phase is directly related to the formation temperature; the lower the reaction temperature the smaller is the grain size. A low reaction temperature is especially important in Nb_3Al since the grain size cannot be refined by subsequent heat treatment and no successful process has been developed to introduce a dispersed oxide phase, such as ZrO_2 , as pinning sites.¹⁵ The proposed process has the advantage of forming Nb_3Al at a low temperature which implies good superconducting properties.

The scope of this study involves a feasibility analysis as to the viability of the process and an attempt to establish the critical parameters involved in the production of superconducting Nb_3Al wires and tapes.

IV. FEASIBILITY STUDY

A. Solid Solutions of Niobium

In the initial attempt to form bulk metastable niobium solid solutions, Nb_{SS}, a series of alloys were made with nominal compositions 27, 23, 20 and 18 at.% Al. Each sample was prepared from powders with purities given in Table I. The desired quantities were weighed and then blended in a glass container with Al₂O₃ pellets for 2 hr. The powder was isostatically pressed into cylinders at a pressure of 345 N/mm². These cylinders were reaction annealed in a high temperature tantalum resistance furnace equipped with an oil quenching bath (see Fig. 3). Since the oil was under a high vacuum, Corning 704 diffusion pump oil was used as the quenching medium to avoid contamination of the furnace. An ice bath surrounded the stainless steel oil pot to maintain a temperature of 0°C. For the reaction anneal the samples were suspended from a tantalum rod and held at 1950°C for 5 min in 100 Torr He and were subsequently quenched in the oil bath. X-ray diffraction patterns were obtained from each sample after quenching by crushing small amounts into powder. A Picker X-ray diffractometer with Ni filtered Cu-K_α radiation was used. Specimens were also prepared for metallographic examination. Only in the 18 at.% Al sample was the single phase niobium solid solution observed. In all other cases both Nb_{SS} and the A-15 phases were present with the amount of A-15 decreasing with decreasing Al content. This result agrees well with the observations of previous investigators.¹⁶ To prove that the 18 at.% Al sample was indeed metastable it was subjected to a low temperature aging at 1000°C for 15 min. Diffraction analysis

of this aged sample disclosed that a large fraction had been transformed to the A-15 phase. A study of the X-ray diffraction patterns revealed a large broadening of the Nb peaks in the as-quenched metastable samples. This is probably a result of composition gradients in the sample. The measured lattice parameter of the metastable 18 at.% Al specimen was 3.277 ± 0.001 . When this sample was aged, the A-15 peaks appeared while the Nb peaks were shifted and decreased in intensity. The lattice parameter of the A-15 was 5.202 ± 0.003 while the Nb lattice parameter had increased to 3.293 ± 0.001 . This established that bulk metastable solid solutions could be obtained by a moderate quenching rate, and that the composition was limited in this procedure to about 18 at.% Al.

The formation of the A-15 phase from the solid solution has been previously described as a massive transformation.¹⁷ In samples higher than 18-19 at.% Al content, a massive transformation was observed at the grain boundaries on quenching. Massive transformation is a type of solid state reaction dependent upon thermal activation and will occur both on heating and cooling. Massive transformation involves local short ranged diffusion of atoms to form a new crystal structure with no apparent composition change. In this case an Al supersaturated Nb matrix transforms by means of a massive transformation to the stable A-15 compound, denoted A-15_m. The quenching rate appears to be one of the main factors in determining the amount of massive A-15_m formed. If the rate of cooling is rapid enough, the high temperature phase will be retained, while at slower rates the equilibrium phases will be formed. The largest amount of A-15_m formed was observed at intermediate quenching rates.¹⁸ Composition is also a factor determining whether

the A-15_m will form. As was seen in the first series of alloys, a solid solution could be retained in an 18 at.% Al sample by rapid quenching, while in a 22 at.% Al sample cooled at the same rate, it was not possible to avoid the formation of the A-15 phase. The closely spaced acicular precipitates shown in Fig. 4a are characteristic of the A-15_m phase formed during the aging of the quenched solid solution. The blunt, massive precipitates in Fig. 4b are formed during the quenching of a sample having an Al content higher than 18 at.%.

Once established that a metastable solid solution could be formed the next step was to obtain an indication of its mechanical properties. The previous method of preparation was not suitable for this type of study as a result of the large percentage of porosity developed in this "sinter react" technique. To eliminate this problem, elemental powders were pressed and then arc melted in a reduced argon atmosphere with a non-consumable tungsten electrode. The samples were individually melted and inverted four times to ensure homogeneity. Nominal compositions of the samples were calculated from careful weight loss measurements. All weight loss was attributed to the evaporation of Al and from previous experience predetermined additions were added so that the desired compositions could be controlled. Good agreement was observed between the composition calculated taking into account the weight loss and the results of microprobe analysis. The arc melted samples were annealed at 1950°C for 10 min to ensure the formation of a homogeneous solid solution. During this heat treatment Al losses occurred and the weight change was measured after oil quenching to redetermine the composition of the samples. This procedure yielded porosity-free samples suitable for mechanical testing such as microhardness and ductility.

B. Mechanical Properties

Since the solid solution extends over a relatively broad range, a study of the microhardness vs composition was expected to give a good insight into the mechanical properties. Therefore, five samples with compositions about 18.5, 15, 11, 6.5 and 3 at.% Al, along with a pure Nb standard were prepared in the manner described above. After processing, X-ray analysis showed that in each case the metastable solid solution had been formed. Slices were then cut with an abrasive wheel and polished for Vickers microhardness testing. The dashed line plot on Fig. 5 shows the results for the as-quenched samples. Up to the 3 at.% Al sample a sharp increase in the hardness is observed. This behavior must be attributed primarily to solution hardening of Nb by Al. There are no other significant means of hardening since there is no stable second phase in this region of the phase diagram. The hardness remains rather constant until above about 11 at.% Al, where another large increase is noticeable. This type of behavior results from an additional hardening mechanism. This seems plausible since the second increase occurs near the composition corresponding to the metastable solid solution. Considering the fact that the A-15 phase is the thermodynamically stable one at this composition, it is quite possible that submicroscopic precipitation has occurred. The presence of these precipitates, similar to G.P. zones in Al alloys, can be positively proven only by transmission electron microscopy. Strong indirect evidence, however, can be obtained in a different manner. If, indeed, the hardening at approximately 11 at.% Al is due to the first stages of precipitation of the A-15 phase, the amount of precipitates

will be dependent upon the quenching rate. Obviously, in slowly cooled samples the equilibrium phases will form. Therefore, by subjecting a similar series of samples, identically prepared, to a slower quenching rate, the percent of the microscopic conglomerates should increase and enhance the shape of the hardness curve. This was done and the results can be seen in the solid line of Fig. 5. There was no quantitative measure of the quenching rate for the first series of samples. In the second series the samples were allowed to cool outside the hot zone for 5 sec before being quenched in oil held at 0°C.

The difference in cooling rates was relatively small, but sufficient to result in a significantly different hardness curve. From this curve it is seen that the increase in the hardness occurs closer to 8 at.% Al, which is the limit of the stable solid solution range. If the second increase in hardness were due to solution hardening, the quenching rate would have had little effect on the hardness. This behavior indicated that the quenching rate is of extreme importance in determining the hardness and by inference the ductility. Since the quenching rate seemed critical, an attempt was made to obtain a quantitative cooling curve representative of this procedure. This was accomplished by taking the 3 at.% Al sample after arc melting and drilling a hole half way through. The tip of a 95% W-5% Re vs 74% W-26% Re thermocouple was embedded in the sample and connected to a chart recorder equipped with a time base coordinate. The samples were heated to the annealing temperature and quenched, while the temperature was continuously monitored. The cooling curve obtained is shown by the solid line curve on Fig. 6. The range of interest lies from about

1950°C to 500°C. Below this temperature the precipitation rate is much too slow to be of any effect. The cooling curve is almost linear from 1950°C to 500°C and a cooling rate of 180°C/sec was determined from its slope. This gives a good indication of the quenching rate in the core of the specimen, while the outer surface was undoubtedly cooled at a higher rate. The samples were only about 0.94 cm in diameter, and no radial gradient of precipitation or hardness was observed. This suggests that the rate difference involved in quenching the core as compared to quenching the surface is small. The quenching rate of the first series of samples was higher but within about 25% of the measured rate. It appears, therefore, that a rather small change in quenching rate resulted in a large increase in hardness.

Continuing the investigation of the mechanical properties, the determination of a stress-strain curve of a standard tensile test would have been appropriate. Unfortunately, the size and shape of the samples precluded this possibility. An alternative method was used from which a measure of the reduction in thickness to fracture could be determined. Flat slices were cut from the quenched samples and their thickness recorded. The samples were then flat rolled until the first sign of cracking appeared. This method was somewhat subjective but puts an upper limit on the ductility. The results, seen in Table II, indicates that the ductility was limited and much lower than had been expected. At the same time the dependence of the microhardness after rolling on composition was checked in order to give an estimate of the work hardening range (see Fig. 5). It is likely that by improving the processing conditions, i.e., the quenching rate, the ductility

might be improved slightly. At this point, however, all indications suggest that any type of processing of the solid solution at room temperature cannot be readily performed.

One sample was rolled at 400°C to see whether the ductility could be substantially changed by warm rolling. The reduction in thickness to fracture was doubled at this temperature. This cannot be readily explained since 400°C is a low temperature as compared to the melting temperature of Nb. Further work needs to be done in this area of elevated temperature deformation. The main restriction is the temperature at which the rate of precipitation of the A-15 becomes rapid relative to the time required for deformation.

C. Twinning and Aging

Two samples with a high percentage (12-15 at.% Al) were aged for 1 hr at 1000°C after rolling. Metallographical examination revealed a striking contrast between the 2 samples. The samples had been processed identically and the only difference was in composition. Referring to Fig. 7 the difference in microstructure is easily observed. In one case, Fig. 7b, large areas of fine needle precipitates are present while in the other, Fig. 7a, what looked very straight Widmanstätten-like precipitates appeared. A Widmanstätten type of precipitation is often a competing mode of formation with a massive transformation of a new phase and is composition dependent.¹⁷ The results of an X-ray analysis which showed the presence of the A-15 phase in both samples seemed to confirm this explanation. It proved, however, to be inconsistent when the same type of Widmanstätten structure was observed in a rolled but unaged sample implying that this structure forms prior to the aging

treatment, and is a result of deformation. Two explanations seemed possible: either strain induced precipitation takes place in this system or that what appeared as precipitates are deformation twins. X-ray diffraction of this unaged sample failed to reveal an A-15 phase. Moreover, when the sample was anodized in dilute NH_3OH , no difference in oxide colors could be seen between the lines and the matrix. Recalling that twinning has been previously observed in pure Nb,¹⁹ it can be concluded that the network of parallel lines represents twins resulting from the deformation.

A brief study of the microstructure of rolled samples with varying Al concentration showed that the amount of twinning is proportional to the composition (see Figs. 8a-c), and is found extensively in samples which are metastable (>8 at.% Al). The presence of the twins is not only interesting in itself, but may play an important role in the final microstructure of the superconductor.

When precipitation occurs it usually begins at a grain boundary or discontinuity. This is a result of the lower thermal energy needed for the formation of precipitates in regions of local misfit. Dislocations and twin boundaries are favorable precipitation sites. Figure 9 shows a comparison between two samples identical in composition after aging for 1 hr at 1000°C . One sample has been only aged (Fig. 9a) and the other rolled prior to aging (Fig. 9b). The twins act as very effective sites for the precipitation of the A-15 compound. This might be a desirable feature for reasons of continuity of the A-15 phase. In order for a superconductor to carry current there must be an electrically continuous network of the superconducting phase. In a twin-free

structure (Fig. 10a) the only continuous A-15 path is along the grain boundary. In the twinned sample of the same composition (Fig. 10b), however, many continuous paths are apparent in the sample. A continuous path can be obtained without twinning by increasing the total Al concentration e.g., an 18 at.% Al sample when aged will transform almost entirely to an A-15 phase. This fixes the lower limit of the Al composition of alloys which can be used without deformation. A continuous A-15 network based on the deformation twins presents an important advantage over the one produced by aging of a non-deformed high Al content alloy. The optimum configuration for a superconductor is in the shape of fine multifilimentary composites. Alternating current losses are reported to be much lower when the size of the transverse dimension of the superconducting filaments is small.²⁰ The twinned A-15 structure seems to approach more closely the desired configuration.

The high magnification photomicrograph (Fig. 11) of the deformation twins shows their wide and irregular boundaries. The marked curvature of the twins formed in a sample which has undergone a large deformation during rolling at 400°C is shown in Fig. 12. The increased ductility noticed when rolling at 400°C might be related to this curved twin phenomenon.

To study the details of the aging process and the formation of the A-15 phase from the solid solution, a Theta Dilatometer was employed. An as-quenched sample was machined with plane-parallel sides and mounted in such a way that its expansion and contraction could be observed as a function of temperature. A small induction heater was used to age the sample while its change in length was

continuously recorded. At temperatures of 800°C and below, the precipitation was too slow to be detectable by this procedure. A 15 at.% Al sample was aged at 850°C and a contraction was observed. This is expected when the A-15 begins to precipitate since Nb₃Al has a higher density than the matrix solid solution. The contraction continued for about 80-90 min and then leveled to a constant value, the aging process appearing to have been completed. However, when the temperature was increased to 1000°C contraction again was observed. This indicated that further precipitation of the A-15 phase had occurred. In order to get a better understanding of the mechanism, a 15 at.% Al sample was aged at 900°C. The contraction, as shown by the dilatometer curve, was completed within 15 min even though the sample was maintained for 60 min at that temperature. A photomicrograph of the sample after this aging treatment is shown in Fig. 13b. Precipitation occurs throughout the sample mainly at the interior of the grains. The sample was then reheated to further age the material, since the amount of A-15 which had precipitated did not correspond to its composition according to the lever rule. This time the sample was aged at 1000°C for 30 min. A photomicrograph of the sample after this additional heat treatment (Fig. 13a) shows increased precipitation, which is essentially complete, since higher temperature annealing did not show any further contraction. These studies showed that the A-15 can be formed from the quenched solid solution at a temperature of 850°C within a reasonable period of time. This conclusion is important since the formation temperature of the A-15 phase is a critical parameter affecting the superconducting properties.

V. PROCESS DESIGN

A. Experimental Set-Up

In the design of any process it is important to perform preliminary studies to establish the variables of the system. The experiments which are done should be representative of the process and easily applicable to the final design. The previous results indicated that the process as it had been carried out presented two main disadvantages: 1. the ductility of the quenched sample was limited; 2. it was not possible to retain a metastable solid solution of alloys having higher than 18 at.% Al content. This second point is important since it has been shown by Kohr et al.¹² that the critical temperature falls off rapidly for Al concentrations lower than 21 at.%. Any process, if it is to be viable, must overcome these two limitations.

Since it appeared that the desired shape could not be achieved after the solution reaction, it seemed necessary to produce the wire or tape shape prior to the heat treatment. In order to achieve this objective a diffusion type process was chosen. Niobium tubing 99.9% purity which had been machined from a rod was used to sheath a 99.99% purity Al rod. The ductility of the composite was such that it allowed easy deformation to a 0.5 mm diameter wires from which 0.25 mm thick tapes were made.

According to the equilibrium phase diagram, Fig. 2, the maximum attainable solid solution is 23 ± 0.5 at.% Al. In bulk form, however, only about 18 at.% Al was retained on quenching. It was presumed that the critical temperature of a 21-22 at.% Al alloy aged at 1000°C would be high and its grain size would be small. It seemed plausible

that by increasing the cooling rate a metastable solid solution with higher Al content could be retained. The process, therefore, was modified to allow a wire or tape sample to be heated to $\sim 1950^{\circ}\text{C}$ and rapidly quenched. Direct resistive heating was used for two reasons. 1. The time of the reaction could be regulated easily from seconds to minutes as desired with the sample reaching the high temperature very rapidly. 2. The sample was gripped in such a way that the ends of the wire were cooled. This eliminated any possibility of the aluminum escaping from the ends. Oil quenching was found to be unsatisfactory as a means of quenching. Therefore, simultaneously with the current being turned off, a jet of high pressure helium gas was directed on the sample from a special quenching set-up. The cooling rate was measured by attaching a W-Re thermocouple to a 0.37 mm niobium tape and quenching from 1900°C . The dashed line on Fig. 6 gives a comparison between the helium and oil quenching rates. The helium cooling rate exceeded the oil cooling rate by a factor of three and is due primarily to the small size of the sample. With this set-up (Fig. 14) samples of about 8 cm in length could be produced.

B. Processing Flat Tapes

The first samples processed were flat tapes. Niobium tubing with O.D. = 5.8 mm and I.D. = 0.95 mm were filled with 0.93 mm Al rod. The composite was swaged down to 1.88 mm and then flat rolled to 0.37 mm in thickness. Sectioning this sample showed that the inner Al core was no longer uniform after the deformation. This is due to the relative softness of the Al core with respect to the Nb tubing. Samples were reacted for 30 sec at a temperature $\sim 1950^{\circ}\text{C}$ and quenched. Metallography

showed that there was a reaction layer, but it was not continuous throughout the 8 cm sample length. Microhardness measurements on the as quenched layer yielded a hardness of 385 VH for the solid solution region which is comparable to that obtained in previous experiments. The sample was deformed slightly and twins could be observed in the reaction zone. Using electron microprobe analysis the concentration profile of Al across the thickness of the sample was determined (Fig. 15b). This graph shows that the reaction layer was about 200 μm thick, with a concentration profile typical of a diffusion type reaction. The main point to be noticed in this curve is the total amount of Al which is in solid solution. An average composition of the center core was determined from several microprobe point analysis measurements to be about 21 at.% Al. This point is noteworthy because it proves that, as anticipated, a higher Al content solid solution was retained by the higher quenching rate. Upon aging it was expected that the 21 at.% Al solid solution would transform into an A-15 phase with the same composition. To prove this point a length of the tape was aged for 1 hr at 1000°C. Micrographs of the as-quenched and aged sample can be seen in Fig. 16. The dependence of the Al composition as a function of the distance from the edge of the aged sample is given in Fig. 15a. Comparing Figs. 15a and 15b it can be observed that during the aging the size of the reaction layer did not significantly increase in thickness. This implies that the mobility of Al atoms at this aging temperature is not sufficient to deplete the core of Al, but is sufficiently high to transform the solid solution into the A-15 phase. Examining the micrograph of the aged tape in Fig. 16b,

two layers can be seen, the center which is essentially single phase A-15 and bordering it a narrower dark layer. Microprobe analysis of the dark layer determined the composition of the edge layer to be about 17 at.% Al. It is believed that this dark layer corresponds to a two phase material where the A-15 and Nb solid solution are finely intermixed.

This first tape, although not successful from the standpoint of processing a long continuous superconductor, gave the answers to many questions. It proved that a solid solution with 21 at.% Al could be retained in a metastable form. Also, when aged a single phase A-15 could be produced on a large scale at a temperature of 1000°C. This temperature is by no means the lowest or the optimal.

C. Continuous Wire Processing

An attempt to process an internally continuous wire resulted in satisfactory samples. The discontinuity of the Al core in the previous flat tape was attributed to the soft Al used. New samples were processed using 2011-T3 Al which is much harder due to the addition of a small percentage of Cu. Wire samples could be produced without difficulty by a combination of form rolling and wire drawing. Micrographs of 0.5 mm diameter wire showed that the Al core was not only continuous throughout the length but also retained its circular cross section. By matching the hardness of the two components, Nb and Al, the mechanical deformation yielded very uniform wires.

An attempt to solution react these wires was unsuccessful because the Al core locally was off center and the reaction layer broke through the wire surface, causing the wire to break. It is necessary to reduce

the Al core size if samples are to be satisfactorily reacted. This can be accomplished by either rebundling the single cored wire or starting with a smaller initial Al rod.

VI. SUPERCONDUCTING PROPERTIES

Critical Temperature

The critical temperature measurement of a material transformed to the A-15 phase from the solid solution gives a good estimate of the potential of this process. It was expected that the T_c of this material would be lower than that of a well ordered stoichiometric A-15. However, if the T_c was lower than 15.5°K, there would be no advantage in this process as compared to that reported by Ceresara.²³

The critical temperature of 3 samples which had been solution quenched and aged for 1 hr at 1000°C, 18 hr at 950°C and 24 hr 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 $17.6 \pm 0.5^\circ\text{K}$ with a transition width of about 1.0°K. There was a 100°C aging temperature difference between the samples but no detectable difference in T_c was noticed. The only variation between the three samples was the amount of signal change measured by the oscillator coil. The 1000°C sample had a very noticeable transition while the 900°C sample transition was quite small. This suggests that the aging time was too short to allow the complete transformation of the solid solution to the A-15 phase in the 900°C aged sample.

This value of T_c is a full 2°K higher than has been reported at formation temperatures below 1000°C. Comparing the values of T_c reported by Kohr et al.¹² (see Fig. 17a), the measured T_c in our material corresponds to that of an A-15 with about 21 at.% Al. This is actually the composition determined by previous microprobe analysis. This consistency suggests that the material formed at a temperature

below 1000°C is well ordered, since Fig. 17a implies a well ordered structure resulting from the long low temperature heat treatment. If this is true, then the lack of dependence of T_c on the aging temperature might be explained. Since the composition of the samples is identical, the change of 100°C for only 24 hr would not significantly affect the atomic order.

With a T_c of 17.6°K this process leads to a practical material which could be developed into a commercial method of fabricating Nb₃Al. A schematic diagram of the process is given in Fig. 18a along with a photomicrograph of the final wire microstructure in Fig. 18b.

VII. DISCUSSION AND CONCLUSIONS

The results of this study indicate that composite wires of Nb and Al can be solution treated, quenched and aged to produce a functional shaped Nb_3Al superconductor at temperatures below 1000°C . The main problem with producing Nb_3Al is related either to phase equilibrium or diffusion kinetics. To achieve a stoichiometric compound the temperature must be above 1500°C , as can be seen in the equilibrium phase diagram. This high temperature prevents the possibility of processing a copper stabilized composite because copper is liquid at this temperature. At lower temperatures, on the other hand, the kinetics are such that the Nb_2Al and NbAl_3 intermetallics are favored over the formation of Nb_3Al .^{21,22}

Other processes have been suggested as a means to fabricate wire from the Nb-Al system. Eagar et al.¹⁵ initially process multifilamentary composites of elemental Nb and Al in exactly the same manner discussed in this report; however, the important difference lies in the subsequent heat treatments. Eagar forms the A-15 phase by direct conversion from the elemental states and then performs a low temperature ordering anneal. With this high temperature diffusion reaction he was able to obtain higher values of critical temperature, $>18^\circ\text{K}$, but was unable to consistently produce high current carrying capacities. He related this to the variation in grain size which was in the range of 1-20 μm within the same sample. In an attempt to improve this problem of reproducibility, lower reaction temperatures were tried, yet no sample below 1500°C had optimum superconducting properties. It appears that the high temperature heat treatment does

not in principle preclude a small grain size and high critical current densities. However, more work is required to reproducibly prepare samples having small grain size. Even if this is accomplished, however, it would not be possible to incorporate copper for stability in his composites due to the high temperature reaction.

Ceresara et al.²³ have recently reported that Nb_3Al has been formed by diffusion at temperatures as low as 750°C . Ceresara reports high critical current densities ($1.5 \cdot 10^5 \text{ A/cm}^2$ at 6.4 T), but the critical temperature is low, 15.5°K . The high current carrying capacity of this material is most probably due to the extremely small grain size achieved during the low temperature reaction. The depression of T_c is most likely a result of the deviation of the A-15 from stoichiometry. For a reaction taking place below 1000°C , the A-15 phase region only extends to 19 at.% Al. There is no way to circumvent this limitation for a straightforward diffusion process in this temperature range. Even though fully stabilized composites can be proposed by this process, the A-15 composition cannot approach stoichiometry.

The method used in the present work should eliminate the grain growth inherent in high temperature reactions and, at the same time, not be limited by the equilibrium phase boundaries since it deals with metastable compositions. This method has two important advantages resulting from the formation of a metastable solid solution: 1. the critical current densities are expected to be high, since the A-15 formation temperature is low; 2. the possibility exists that, prior to forming the A-15 phase, the as-quenched solid solution composite can be cabled with copper. This is possible since the solid solution can withstand

plastic deformation without disturbing the continuity of the reaction layer, and the subsequent aging temperature is below the melting point of copper.

It is concluded that further development of this process could lead to the fabrication of a high T_c , high J_c , fully stabilized Nb_3Al superconductor.

VIII. AREAS OF FUTURE STUDY

Since this work represents the initial study of the process involving the formation of metastable Nb-Al composites, there are a vast number of areas open to further investigations and optimizations. At this point the critical current densities as a function of applied magnetic field have not been determined. It is of utmost importance that these values be measured, because if the current densities are high as expected, the process becomes commercially realizable. The critical current measurements can also be used to optimize the aging temperature. As was discussed previously, T_c is not strongly dependent upon aging temperature, but J_c could very definitely be influenced by the aging temperature. This dependence, if substantial, should be determined as a function of grain size.

This process is not limited to single cored conductors, but can easily be adapted to multifilamentary composites. This possibility should be investigated and properties related to filament thickness.

Another interesting area of further investigation is the effect of deformation of the as-quenched wire prior to aging. As shown in Section IV, extensive twinning takes place in this system. Preliminary experiments show that twins can be produced in the reaction layer. It might, therefore, be possible to form an interconnected network of the A-15 phase in the superconducting wire as a result of the deformation twins. This could result in a filamentary morphology without the added step of bundling single cored wires.

The composition of the solid solution is a very critical parameter, and depending upon the initial Nb and Al core size, the solution

reaction time will vary. It is important to determine this relationship in order to successfully reproduce sample properties.

At present, the composition of the metastable solid solution is about 21 at.% Al. According to the phase diagram 23 at.% Al can in principle be retained in solid solution. This might be achieved by, either further increasing the quenching rate, or by alloy additions which shift the phase boundaries toward the Al rich end. Increasing the effectiveness of the quench might be accomplished, for example, by using liquid N_2 rather than He gas. Alloy additions, on the other hand, which will not affect the superconducting properties but at the same time shift the phase boundaries, may be difficult to find. Elemental Ga and In were added to aluminum powder in a preliminary attempt to increase the Al content of the solid solution but neither was found to be useful. Finally, when these above parameters are determined, an attempt should be made to produce long wires on a continuous basis.

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Table I. Source materials used.

Material	Source	Nominal Purity	Form
Al	Contronics	99.99	Powder (-400)
Al	United Mineral and Chemical	99.999	Rod
Al	A. M. Castle	5.5 Cu, 0.5 Bi, 0.5 Pb	Rod
Nb	Fansteel	99.9	Rod
Nb	Wah Chang Albany	99.9	Powder (-325+400)

Table II. Ductility of as-quenched samples.

Sample	At.% Al	Initial Thickness (mm)	Final Thickness (mm)	Temperature During Deformation	% Reduction in Thickness
750617-A	15	0.023	0.021	20°C	7.6
750617-C	16	0.034	0.032	20°C	6.6
750617-C	16	0.0185	0.015	400°C	16.2

FIGURE CAPTIONS

- Fig. 1. The Nb_2Al structure.
- Fig. 2. The niobium-rich region of the Nb-Al phase diagram as proposed by Lundin and Yamamoto.¹⁶
- Fig. 3. Abar furnace. 1. Extension tube, 2. Tantalum rod, 3. back filling port, 4. electrical leads, 5. tantalum heating element, 6. specimen, 7. radiation shields, 8. water cooled wall, 9. vacuum connection, 11. stainless steel oil pot, 12. Dow Corning 704 Diffusion pump oil, 13. ice bath.
- Fig. 4. (a) Acicular needles of A-15 formed massively at 1000°C.
(b) Blunt A-15 formed massively on quenching from 1950°C.
- Fig. 5. Plot of hardness vs at.% Al.
- Fig. 6. Plot of quenching rate of oil bath and helium jets.
- Fig. 7. (a) Widmanstätten type structure of a sample of ~12 at.% Al aged at 1000°C. (b) Acicular needles of A-15 of a sample of ~15 at.% Al aged at 1000°C.
- Fig. 8. (a) Twins observed after rolling an as-quenched 18 at.% Al sample. (b) Twins in a 15 at.% sample rolled after quenching. (c) Twins in a 12 at.% sample rolled after quenching.
- Fig. 9. (a) Quenched and aged 1000°C at 15 at.% Al sample. (b) Quenched rolled and aged 1000°C at 15 at.% Al sample.
- Fig. 10. (a) Same as 9(a). (b) Same as 9(b).
- Fig. 11. Twins in a 15 at.% Al sample formed by rolling at room temperature after quenching.
- Fig. 12. Twins in a 15 at.% Al sample formed by rolling at 400°C after quenching.

- Fig. 13. (a) Microstructure of a 15 at.% Al sample aged 1 hr at 900°C and then 30 min at 1000°C. (b) Microstructure of a 15 at.% Al sample aged 1 hr at 900°C.
- Fig. 14. Experimental set up with specimen wire and quenching valves in place. (a) Current leads, (b) water cooled wall, (c) wire specimen and (d) quenching valve.
- Fig. 15. (a) Electron microprobe data plot of a flat tape sample resistively heated to 1950°C, quenched and aged for 1 hr at 1000°C. (b) Microprobe data plot of the same tape prior to aging.
- Fig. 16. (a) Photomicrograph of flat tape as-quenched Vickers hardness of core = 385 and of Nb sheath = 190. (b) Photomicrograph of flat tape aged 1 hr at 1000°C Vickers hardness of core = 890 and of Nb sheath = 150.
- Fig. 17. (a) Process flow chart. (b) final microstructure of Nb₃Al composite wire.
- Fig. 18. (a) Dependence of T_c on composition as reported by Kohr et al.¹² with present data point. (b) T_c plot measured inductively on a wire sample aged 1 hr at 1000°C.

THE A-15 STRUCTURE

XBL 7511-7276

Fig. 1

XBL 7511-7575A

Fig. 2

XBL 7210-7043 A

Fig. 3

(a)

(b)

XBB 7511-8533

Fig. 4

Fig. 5

XBL 7511-7573

XBL 7511-7574

Fig. 6

(a)

(b)

XRB 751J-8537

Fig. 7

(a)

(b)

(c)

Fig. 151-152

(a)

(b)

XPB 7511 8985

Fig. 9

(a)

(b)

7511-8536

Fig. 10

Fig. 11

Fig. 12

XRB 7511-8539

(a)

(b)

XMR 7511-8538

Fig. 13

Fig. 14

XBL 7511-7582

Fig. 15

(a)

(b)

XBB 7511 8534

Fig. 16

(a)

(b)

Fig. 17

XBR 7511-8540

(b)

Fig. 18