Metallurgical Considerations for Optimizing the Superconducting Properties of Nb_3Al

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The effects of heat treatment and composition on the superconducting transition temperature of Nb_3Al were studied in conjunction with an X-ray diffraction investigation of ordering and other structural effects. It was determined that an ordering anneal of 750°C for at least 48 hr achieved a maximum midtransition T_c of 18.5 K in arc-melted samples of Nb_3Al. The changes in lattice parameter and order parameter during heat treatment indicate that the β-tungsten crystal structure becomes more ordered as the maximum T_c is approached. Further, the T_c of 18.5 K could not be reached in Nb_3Al material having nonstoichiometric composition. In such material, there was a direct correlation between increasing percentage of second-phase Nb_2Al present and decreasing T_c after the maximum T_c had been obtained. The information obtained during this investigation led to the development of a simple empirical model to explain the change in the T_c of Nb_3Al. Also based on this work, a method was evolved for producing conductor material based on the high T_c Nb_3Al alloy (Appendix I).

HIGH critical current density, high critical field, and high critical transition temperature superconductors are of interest because of the obvious practical economic benefits these properties can make to potential applications. For instance, operation at 12.0 K rather than 4.2 K brings a threefold increase in the Carnot efficiency of the refrigeration system being used. In most cases, the necessary high T_c alloys have a brittle β-tungsten or rock salt crystal structure, making them difficult to fabricate into any useful configuration. The majority of development work to-date has been completed using Nb_3Sn. Kunzler *et al.*[1] and Olsen *et al.*[2] used a powder core wire process in which niobium and tin powders were mixed and packed into a niobium tube, drawn into a fine wire and sintered into a Nb_3Sn phase by heating the wire at elevated temperatures. Later Hanak *et al.*[3] used a halide vapor deposition process in which niobium and tin were codeposited in a 3:1 atomic ratio onto a stainless steel, platinum, or quartz substrate to form a continuous Nb_3Sn phase. Other processes[4-6] have been attempted which form a reaction layer of Nb_3Sn by coating the surface of niobium tape with tin which was then diffused into the niobium by heat treatment. A variation of this method was attempted by Tachikawa and Fukida.[7] They imbedded niobium in a tin matrix which could then be drawn into a fine wire and heat-treated to allow the tin to diffuse into the niobium to form an Nb_3Sn reaction layer on the surface of the niobium wires. Other processes have been attempted with varying degrees of success.

It is the purpose of this investigation to study the metallurgical and superconducting properties of Nb_3Al, a β-tungsten structure superconducting alloy having a T_c of 18.5 K and a critical field at 4.2 K in excess of 300 kG;[8] and if possible, use this information to develop a process for fabricating the material into a configuration that can be used in a practical superconducting device.

The prime consideration for optimizing the superconducting properties of Nb_3Al is how various heat treatments affect the material's β-tungsten structure. In the ideal formula, A_3B, for the general β-tungsten structure, the A atoms occupy half the tetrahedral of (1/2, 1/4, 0) sites in a B atom bcc lattice. The resulting arrangement of atoms leads to a unique crystallographic feature in that the A atoms form three orthogonal close-packed rows or chains parallel to the edges of the unit cell. These A chain atoms are squeezed together, implying both an anisotropic density of states and a high electron-phonon interaction along each chain. Either of these factors may lead to a high T_c. Although the correct explanation for a high T_c is not known, it is thought that any alteration in the orthogonal A chains can greatly affect the resultant T_c. The disruption of the A chains may occur by a classical order-disorder transformation,[9,10] by point defects occurring during annealing,[11,12] or by adding either excess A or B atoms to the A_3B alloy.

Sahm and Pruss[13] have verified the importance of correct stoichiometry to maximum T_c of "Nb_3Al," and found that annealing at 750°C for up to 19 hr would increase T_c more than annealing at higher or lower temperatures. Willens *et al.*[14] have noted that "further heat treatment" of Nb_3Al is necessary to raise the start of the transition from 17.5 to 18.8 K.

EXPERIMENTAL PROCEDURE

Samples of Nb_3Al having compositions ranging from 8.0 wt pct (23.0 at. pct) to 12.0 wt pct (32.0 at. pct) Al were prepared by mixing elemental powders of niobium and aluminum, compacting at a pressure of 36,000 psi into cylindrical buttons 0.50 in. in diam and then arc-melting in a purified and gettered argon atmosphere using a nonconsumable electrode. Each button was remelted three times. Metallography showed minimal

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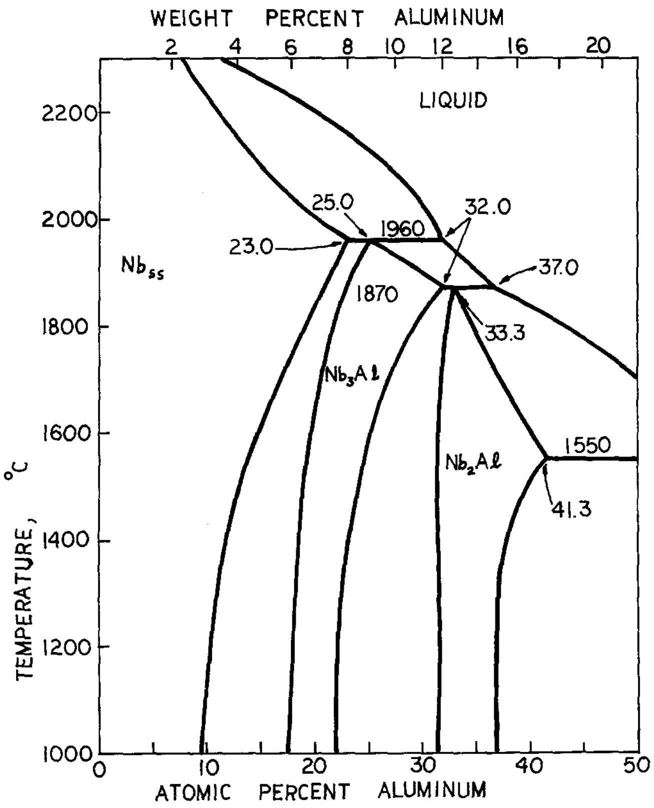

Fig. 1—The niobium-rich region of the Nb-Al phase diagram as proposed by Lundin and Yamamoto.[13]

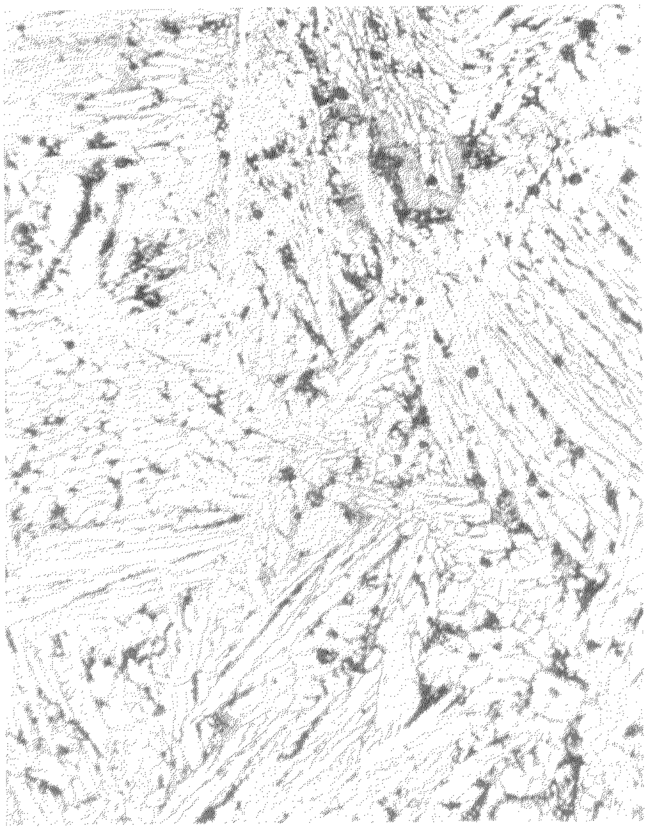

Fig. 2—Microstructure of a stoichiometric Nb_3Al arc-melted sample. Annealed 1 hr at 1750°C, 24 hr at 750°C. The dark phase is Nb_2Al. Magnification 200 times.

segregation as might be expected from an arc-melted, copper-chilled sample. Successive heat treatment of most of the arc-melted samples was carried out for 1 hr at pressures below 5×10^{-5} torr. Weight loss was less than 0.1 at. pct Al. Each sample was wrapped in niobium foil to help prevent contamination. The Nb-Al phase diagram, Fig. 1,[15] indicates that this anneal, together with rapid cooling can be used for a range of compositions to insure that the samples treated would be single phase. All samples, either arc-melted or arc-melted and homogenized were submitted to a low temperature "ordering" anneal at temperatures ranging from 600° to 900°C, for times of 12, 24, 48, and 96 hr. Samples were wrapped in niobium foil and placed in a quartz tube attached to a high-speed vacuum system which could maintain a pressure less than 10^{-6} torr in the tube during the desired anneal. No weight loss was observed.

After all heat treatments were completed each sample was powdered for testing. Because the material was extremely brittle, fine particle powder was easily obtained. Critical temperature measurements were made on +200 mesh powder using a susceptibility technique. By carefully placing the sample in good thermal contact with a calibrated germanium thermometer the sample temperature could easily be measured to within 0.1 K.

X-ray diffractometer samples were prepared of −325 mesh powder samples using standard techniques. Diffractometer patterns of these samples were obtained using a G. E. XR5-D X-ray machine. The diffractometer pattern from the 110 peak to the 321 peak was studied to determine the phases present while only the high angle peaks were studied to determine the lattice parameter. A counting technique was used to determine the relative intensity of the (211) and the (210) peaks. The ratio of these two peak intensities was used to find the degree of ordering for each sample.

A planimetric technique was used to determine the relative intensities of the (411)-100 pct peak of Nb_2Al and the (211)-35 pct peak of Nb_3Al. With this data and a computer calculation of the structure factors, the percent of Nb_2Al phase was determined.

Metallographic specimens were prepared using standard techniques. The results agree with those of Lundin and Yamamoto.[15] A typical microstructure is given in Fig. 2.

Because the measurement of the resistive critical field vs temperature[16] and the critical current density vs applied parallel magnetic field[17] for short lengths of Nb_3Al conductor material have been determined previously, the detailed description of their development and fabrication is given in Appendix I.

RESULTS

Stoichiometric samples were annealed for various times and temperatures to determine the optimum heat treatment. Fig. 3 shows the variation of the midtransition T_c with annealing time and temperature, and also the variation of order parameter with time at 750°C. From this data an optimum annealing temperature of 750°C for samples of the stoichiometric composition was determined. Arc-melted and homogenized samples of nonstoichiometric compositions were annealed at 750°C for 96 hr; this treatment also produced the high-

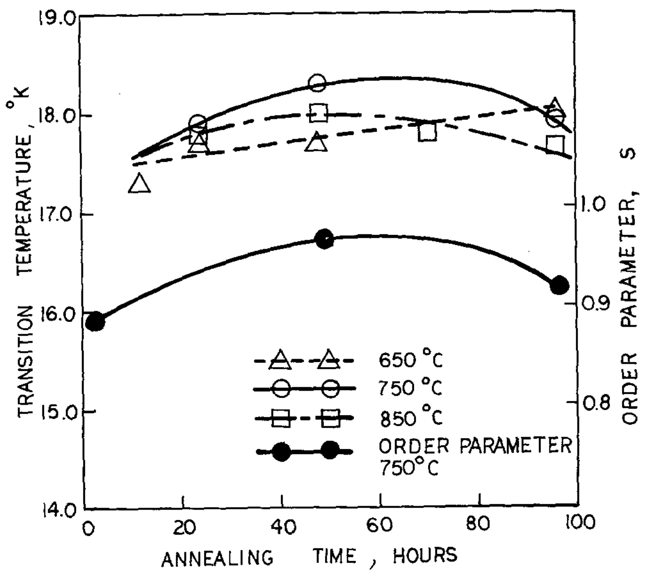

Fig. 3—Dependence of the T_c and order parameter S of arc-melted stoichiometric Nb_3Al on annealing time and temperature. Points shown indicate the midpoint of the superconducting to normal transition.

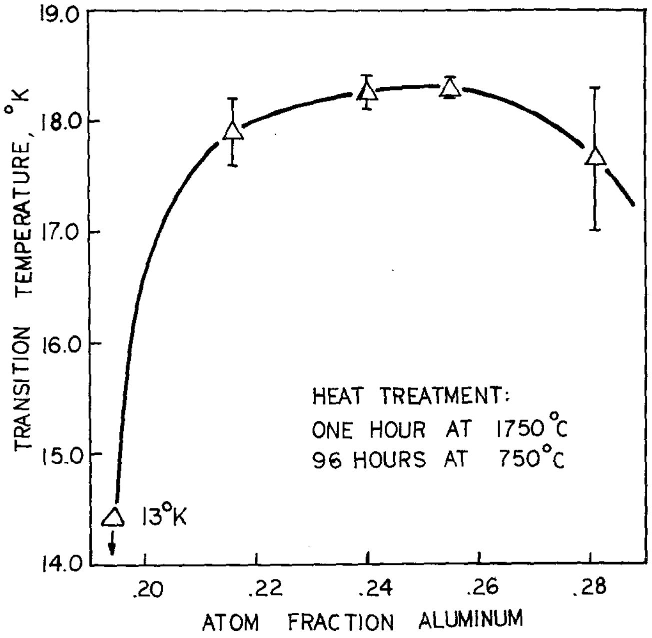

Fig. 4—Dependence of the T_c on composition. Samples were treated for 1 hr at 1750°C and 96 hr at 750°C. Error bars denote transition width.

est T_c in such cases. The variation of T_c with composition for such "optimized" samples is shown in Fig. 4. A maximum T_c exists at the stoichiometric composition. As may be observed in the Nb-Al phase diagram, Fig. 1, second-phase Nb_2Al should precipitate out during long anneals at 750°C. This is born out in Fig. 5 which shows the variation of the percent of Nb_2Al present in an arc-melted (but not homogenized) stoichiometric sample having undergone various anneals. Also shown in the figure is the variation of T_c. Note that the sample having a minimum percent Nb_2Al present has the highest T_c.

In an attempt to determine the mechanism occurring during the ordering anneal, the order parameter was

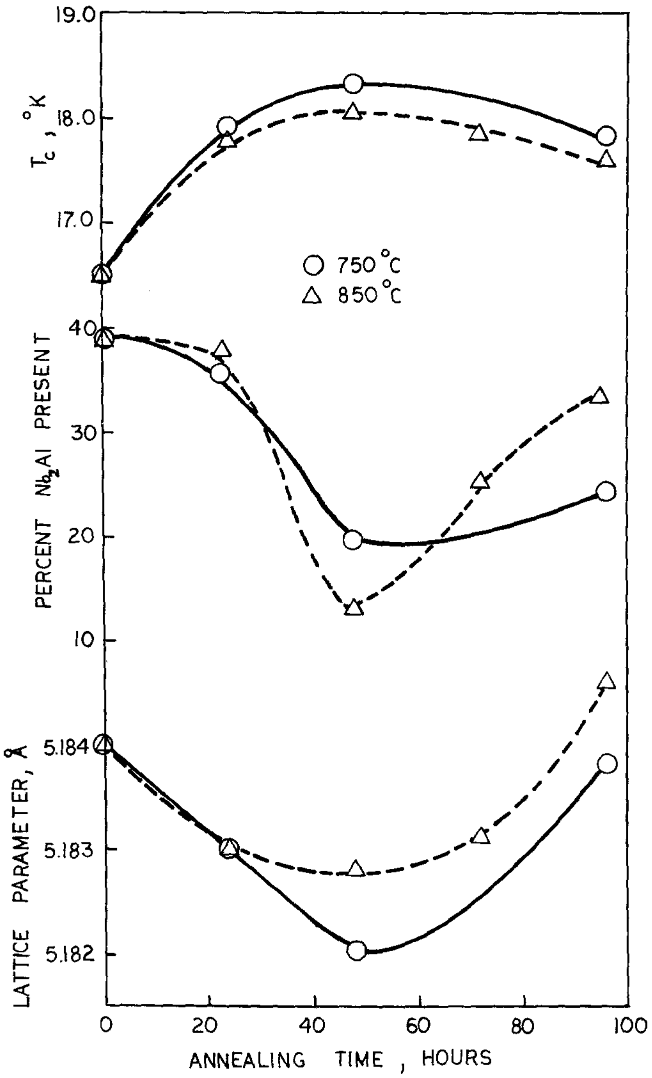

Fig. 5—Variation of the percent of Nb_2Al phase present with annealing time and temperature in an arc-melted stoichiometric Nb_3Al sample. Upper curves show the variation of the T_c of these samples. Lower curves show the variation of the lattice parameter of the samples.

determined for samples having various compositions. This data is compared to the maximum theoretical values in Fig. 6. In all cases a degree of maximum ordering consistent with composition has been achieved. Samples of a particular composition having the maximum order parameter have the highest T_c. To obtain more information regarding the mechanism for optimizing T_c, the lattice parameter was determined for some samples using the method described by Parrish and Wilson.[18] The variation of lattice parameter with annealing time and temperature is shown in Fig. 5. Note that the minimum lattice parameter corresponds to the optimum T_c.

DISCUSSION

Although vacancies have been cited[11] as having a major influence on T_c, we rule this possibility out as a primary mechanism in this particular case. It may be noted, Fig. 5, that the samples having the minimum lattice parameter have the highest T_c, implying a possible increase in vacancies during heat treatment, however the changes in lattice parameter observed imply relatively huge vacancy concentrations. No weight loss was observed during processing indicating that no appreciable aluminum evaporation could occur and give rise to any type of vacancy structure. Also, in general, a low temperature anneal will reduce the equilibrium vacancy-fraction which may have resulted during quenching after a high temperature heat treatment. In view of Fig. 6, we can however make a strong case for ordering. In all cases optimal ordering for a particular composition gave the highest T_c. Having slightly larger niobium atoms in aluminum sites would tend to strain the unit cell. This could increase the lattice parameter and disrupt the continuity of the A chains existing in the crystal structure. The dependence of T_c on atomic ordering in 26 low-T_c β-tungsten compounds has been explored by Hein *et al.*,[19-21] with the general conclusion that the Bragg-Williams order parameter and T_c go up simultaneously, and that a well-ordered β-tungsten structure is most favorable to superconductivity.

However for Nb_3Al a direct equilibrium approach to the well-ordered structure is not possible because the niobium-rich composition, roughly Nb_4Al, not the stoichiometric composition, is stable at the optimum ordering temperature of 750°C, see Fig. 1. Thus the structure having the highest T_c corresponds to an intermediate step on the path to equilibrium, and to persist with the ordering anneal of the stoichiometric alloy leads to the precipitation of Nb_2Al and an aluminum-deficient matrix. The 750°C "optimum" annealing temperature as observed by Sahm and Pruss[13] is optimal only when annealing time is limited. It may be possible to use alloys on the aluminum-rich side of stoichiometry, stopping the precipitation-ordering anneal at the point where the matrix reaches the Nb_3Al composition. However, this would probably require long anneals and the resulting matrix may have too large a composition gradient to be well-ordered.

Therefore it seems that two separate mechanisms are operating simultaneously during annealing of Nb_3Al: one which acts to raise the T_c and one which acts to decrease it. On arc-melting or reacting niobium and aluminum to form Nb_3Al, the material exists in a disordered phase, possibly having some vacancies due to the quench from high temperature. During the initial hours of the 750°C ordering anneal, diffusion takes place reducing the vacancy fraction of the material and increasing the degree of order. Also during this period, second-phase Nb_2Al is trying to precipitate out in the grains as predicted by the phase diagram. However at this time Nb_2Al exists primarily in the grain boundaries and provides niobium and aluminum atoms necessary to fill vacancies and aid in ordering. After annealing for approximately 48 hr the optimum properties for maximizing T_c have been achieved. If a longer annealing time is used, the T_c begins to drop due to the increased effect of the precipitation of Nb_2Al in the grains of the material. The precipitation of this phase will deplete the parent Nb_3Al phase of aluminum, leaving vacancies to be filled by niobium atoms. Because the niobium atom is slightly larger than the aluminum atom this disorder will cause the lattice parameter to increase, Fig. 4. Also the presence of a niobium atom in an aluminum site tends to disrupt the orthogonal A chains running through the β-tungsten structure material thus degrading the material's T_c. The arguments presented above for ordering are probably applicable to the other high-T_c β-tungsten superconductors as well.

CONCLUSIONS

1) The transition temperature for superconductivity of Nb_3Al increases directly with the order parameter.

2) The decrease in optimum T_c caused by nonstoichiometric composition is due to the limitation on the order attainable.

3) Vacancies do not appear to be connected with T_c in this work in any major way.

4) The highest T_c coincides with the lowest lattice parameter.

5) Although the stoichiometric composition is not stable at the optimum ordering temperature (750°C), the well-ordered stoichiometric compound may be attained and precipitation of Nb_2Al avoided by limiting the annealing time.

6) In this case, the degradation of the T_c of Nb_3Al during prolonged anneals is caused by the precipitation of Nb_2Al.

APPENDIX I

DEVELOPMENT OF Nb_3Al INTO A USABLE FORM

First attempts to form a reaction layer of Nb_3Al involved a number of Nb-Al composite configurations including: 1) aluminum tube swaged on to niobium rod, 2) niobium tube swaged on to aluminum rod, 3) aluminum powder packed into niobium tube. In all cases the reduction in area due to swaging was large enough to insure that the niobium and aluminum were in intimate contact with no intervening oxide layer. These configurations were heat-treated at temperatures ranging from 600° to 1000°C for times as long as 300 hr. In all cases only the T_c of niobium was observed. A high temperature heat treatment (above 1870°C) was necessary to guarantee the formation of Nb_3Al when the exact starting composition was unknown.

Therefore short samples comprised of a Nb_3Al coating on a niobium substrate were fabricated by coating niobium foil strips with aluminum, heat-treating at between 800° and 900°C to allow a diffusion layer to form and reacting at above 1870°C for 8 to 15 sec to form the Nb_3Al layer. Aluminum was applied to the niobium strip by resistively melting aluminum wire and allowing it to wet the strip's surface or by evaporating aluminum on to an annealed niobium substrate. A third method of forming an aluminum coating on a niobium strip made use of the metalliding process described by Cook.[22] In this case, aluminided niobium samples having Nb-Al diffusion layers of thicknesses ranging from 0.0005 to 0.0015 in. were obtained from Dr. Sol Musikant of the General Electric Company Re-Entry and Environmental Systems Division (Philadelphia, Pa.) through Dr. Bruce Strauss of the National Accelerator Laboratory (Batavia, Ill.). All of the samples had a resistive T_c of around 9.5 K before heat-treating above 1870°C.

The high temperature reaction anneal was carried out on samples of niobium having an aluminum diffusion layer obtained by the three methods described above. These samples were heated resistively to well

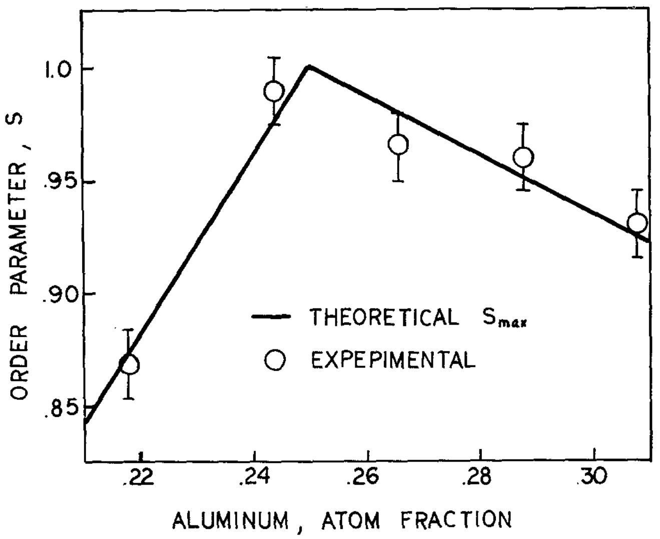

Fig. 6—Comparison of the experimentally-determined order parameter with the theoretical maximum order parameter for various compositions of arc-melted and annealed Nb_3Al at optimum annealing conditions (48 hr at 750°C). Error bars indicate a 2.0 pct experimental error.

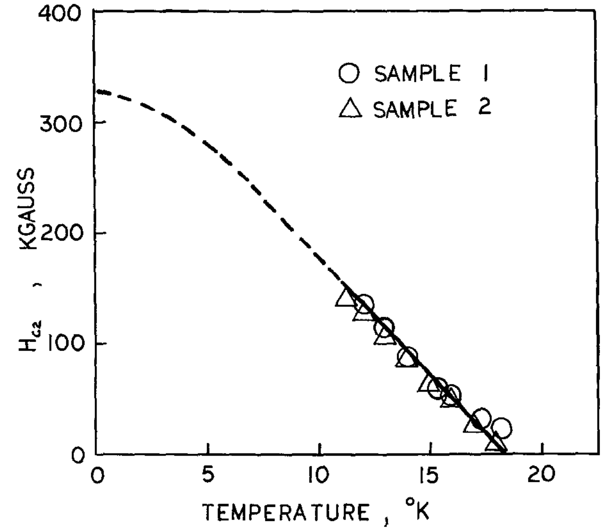

Fig. 7—Upper critical field, Hc_2, vs temperature for a Nb_3Al layer on a niobium tape substrate. Applied field is parallel to sample current.[14]

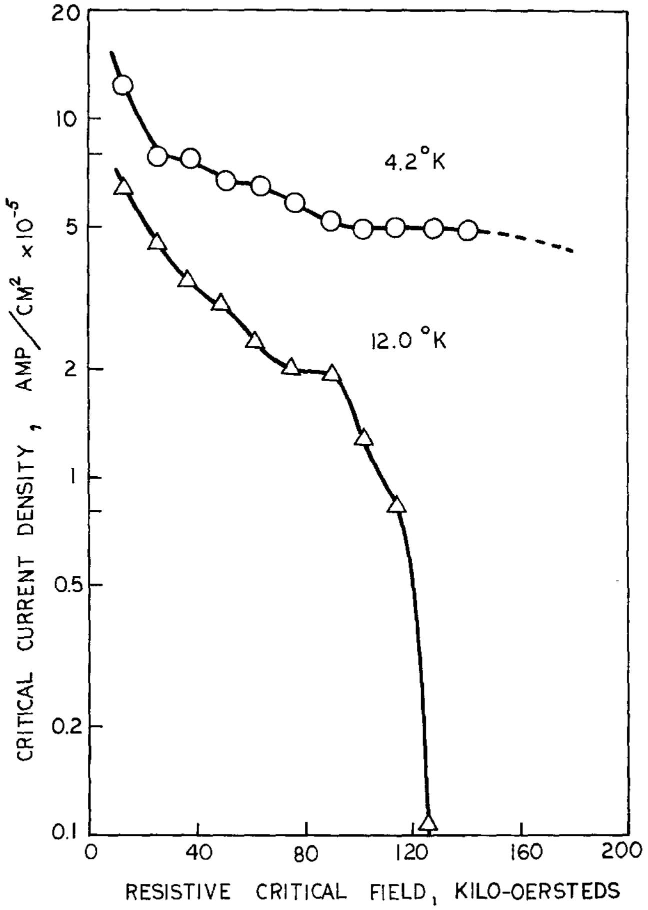

Fig. 8—Variation of the critical current density of a Nb_3Al layer on a niobium tape substrate with applied parallel magnetic field for sample temperatures of 4.2 and 12.0 K.[15]

above 1870°C in a vacuum of below 10^{-6} torr for 8 to 15 sec. The temperature was set by applying 80 to 90 amp to strips having a cross-sectional area of approximately 1.25×10^{-3} sq in. Although the exact temperature was not known, it was determined to be sufficient to form a surface layer of Nb_3Al. These reacted samples were then annealed in a dynamic vacuum at 750°C for 48 hr to optimize the superconducting properties of the superconducting layer.

After all heat treatments were concluded the samples were prepared for measuring their resistive superconducting properties by attaching voltage and current leads in a four-point probe configuration using indium solder and ultrasonic soldering techniques. The sample was then placed in good thermal contact with a calibrated germanium thermometer and placed in a copper tube having a heater wire noninductively wound around it. The tube and sample were then suspended in a glass tube backfilled with helium exchange gas, which was then placed in the liquid helium bath. By adjusting the current in the heater wire the heat leak to the bath could be controlled to set the sample temperature at values above 4.2 K. In this manner the T_c of each sample could easily be determined. By inserting this apparatus in a Bitter-type solenoid (National Magnet Lab, Cambridge, Mass.) with the sample parallel to the applied field, both the variation of the resistive critical field with temperature and the variation of the resistive critical current density with applied field at 4.2 and 12.0 K could be determined. The results of these measurements as shown in Figs. 7 and 8 have been reported previously.[16]

The samples tested could be bent around a 2 to 3 in. radius with no loss in superconducting properties. Thus we have provided a first step toward the production of high temperature superconducting devices from this material.

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