MASTER

CONF-760829--51

METALLURGY, FABRICATION, AND SUPERCONDUCTING PROPERTIES OF MULTIFILAMENTARY Nb_3Al COMPOSITES

J. W. Hafstrom

Applied Superconductivity Conference
Stanford, California
August 16-20, 1976

EB

UofC-AUA-USERDA

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Operated for the U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION under Contract W-31-109-Eng-38

METALLURGY, FABRICATION, AND SUPERCONDUCTING PROPERTIES OF MULTIFILAMENTARY Nb_3Al COMPOSITES*

J. W. Hafstrom†

ABSTRACT

The control of metallurgical structure during fabrication that will improve the superconducting properties of multifilamentary, aluminium-stabilized, Nb_3Al composites is described. Composites are fabricated by placing niobium rods in an aluminum matrix, and then drawing to wire. Nb_3Al is formed at temperatures exceeding 1800°C for ~ 5 s and ordered at 750°C for 48 h. A critical current, $J_c(H)$, in excess of 10^5 A/cm^2 ($F_p \sim 7 \times 10^8$ dynes/cm^3) at 7 T and a T_c to 18.2 K are obtained. Attempts to improve $J_c(H)$ by controlling the grain size in the Nb_3Al diffused layer are discussed. Precipitates, arising from the addition of carbon during Nb_3Al layer growth, do not appear to be effective as grain-boundary or flux pinners. When 1% Zr is added to the Nb, the growth of the Nb_3Al layer is accelerated, T_c is lowered and $J_c(H)$ is not significantly improved. $J_c(H)$ rapidly decreases with an increase in Nb_3Al or $(Nb-Zr)_3Al$ layer thickness, d. $J_c(H)$ is independent of d in composites with $d \gtrsim 1.5$ μm. In general, the Nb_3Al grain size appears comparable to d for $d \leq 1$ μm. Significant improvement of $J_c(H)$ for Nb_3Al superconducting composites reacted at temperatures above 1800°C (to achieve $T_c > 17$ K) is achieved only by maintaining the layer thickness well below $d \sim 1.0$ μm.

I. INTRODUCTION

Transport of sizable, $>10^5$ A/cm^2, currents in high magnetic fields must be achieved in A-15 materials by reconciliation of the need to maintain both high transition temperatures, T_c, and critical fields, H_{c2}, and the need to introduce flux-pinning sites in the material. The high flux-pinning force, $F_p(H)$, required for large current densities in alloy superconductors is achieved by means that are often incompatible with the requirements of order and stoichiometry in A-15 compounds. Grain boundaries are one of the few controllable structural defects in A-15 compounds that do not adversely affect T_c yet offer sufficiently high $F_p(H)$ to be effective as flux pinners. To produce sufficient grain-boundary area for effective pinning, a grain size <0.5 μm is necessary. The paramount problem for the fabricator of Nb_3Al wire is to control the grain size during growth of the Nb_3Al layer at temperatures in excess of 1600°C.

A number of attempts have been made to fabricate Nb_3Al superconducting wire. Eagar and Rose[1] have fabricated multifilament composites (Al fibers in an Nb matrix) reacted at 1700°C. They report $J_c \sim 10^4$ A/cm^2 at $H > 3$ T and Nb_3Al grain sizes to 100 μm. Müller[2] has fabricated Nb_3Al as monofilament wire by reacting Al-coated Nb wire at 1880°C in argon that contained dopants. He reports $J_c \sim 10^5$ A/cm^2 at $H < 7$ T and grain sizes of ~ 25 μm.

We describe studies of a potentially practical method for the production of high-$J_c(H)$ Nb_3Al multifilamentary wire. Emphasis is placed on the metallurgical factors that influence the superconducting properties.

II. PROCESS

In the Nb-Al system, the A-15 phase has a broad region of homogeneity; however, the stoichiometric compound is stable only at temperatures above 1600°C. Nb_3Al can also be formed below 1600°C by sputtering and diffusion under special conditions, but T_c is degraded by the lack of a fully developed ordered structure. Formation of high T_c Nb_3Al superconducting layers by diffusion requires a temperature between 1870 and 1960°C. This temperature range is above the Nb_2Al peritectic temperature and avoids the formation of a stable sigma phase. A rapid quench is necessary to inhibit the precipitation of Nb_2Al from the Nb_3Al. The degree of order in the Nb_3Al is improved by a low-temperature heat treatment that limits the precipitation of Nb_2Al and increases T_c by ordering Nb_3Al more fully.

Multifilamentary composites were fabricated by assembling seven Nb rods in an aluminum matrix encased in an Nb jacket, swaging to wire, and heat treating in an induction furnace to form Nb_3Al by diffusion of Al into Nb. The use of an induction furnace, an industrially feasible approach amenable to fabrication of long lengths of wire by a continuous process, allows the short reaction times necessary to minimize the thickness of the Nb_3Al layer. A reaction temperature of 1900°C can be achieved, held a short time, and the sample rapidly quenched. Temperature is monitored by optical pyrometry. An atmosphere of Ar minimizes evaporative Al loss, decreases the quench time, and transports the dopant gas (C_2H_4). Details of the process are found in Ref. 3.

Monofilament wires were fabricated to study the details of Nb_3Al formation. The Nb or Nb-1% Zr wire was dip-coated (thickness ~ 40 μm) with aluminum in high-purity argon and reacted in an atmosphere of flowing argon or Ar + 0.5% C_2H_4. An ordering heat treatment at 750°C for 48 h was performed after the diffusion heat treatment for these as well as the multifilamentary samples.

Control of the Nb_3Al grain size at temperatures near 1900°C was attempted by minimizing the reaction time that is consistent with the attainment of high T_c materials. The Nb_3Al layer thickness is reduced and smaller grains are expected. Retardation of grain growth may also be possible by introducing a dispersion of fine particles to pin the grain boundaries. However, the particles must not coarsen during the time at reaction temperature.

Nucleation sites for Nb_3Al growth as well as grain-boundary pinning (by formation of nonoxide dispersions) may be altered by the addition of 1% Zr to the Nb wire. ZrO_2 is a poor grain-boundary pinner in Nb_3Al because, at 1900°C, the free energy of formation of Al_2O_3 is comparable to that of ZrO_2 and both oxides will coarsen at the reaction temperature. Carbon, introduced as C_2H_4

Manuscript received August 17, 1976.

*Work supported by the U. S. Energy Research and Development Administration.

†Argonne National Laboratory, Argonne, Il 60439.

in the Ar gas, will form compounds with Zr, but not Al, at temperatures above 1400°C. Coarsening may be controlled by the amount of dopant introduced. Carbon does not enter the A-15 structure.

III. RESULTS AND DISCUSSION

Transition Temperature and H_{c2}

T_c was measured inductively, and the results are listed in Table I. The (Nb-1% Zr)$_3$Al samples consistently exhibited a T_c $\sim$0.6 K lower than the Nb$_3$Al samples. Substitution of Zr for Nb in the chain structure of the A-15 lattice has been shown to lower T_c by 0.6 K for each 1% Zr addition.[4] The presence of carbon does not affect T_c. Thus, evidence exists that much of the Zr has entered the A-15 structure rather than forming carbides.

T_c was broad, up to 5 K in width, for thin Nb$_3$Al layers. The bulk of the material was always superconducting above 16 K. The highest T_c and the sharpest transitions, $\Delta T_c < 0.5$ K occurred in the thickest (Nb-1% Zr)$_3$Al or Nb$_3$Al layers. H_{c2} was >30 T for samples with $T_c > 17.5$ K. The short reaction times used to achieve thin layers result in a degraded A-15 compound either by incomplete ordering or the presence of sharp aluminum concentration gradients within the diffused layer. The A-15 structure is retained in the Nb$_3$Al layer, but only a narrow region may be stoichiometric. The A-15 homogeneity region extends from 23 to 30% Al at 1900°C, and within this range T_c can vary by 10% and H_{c2} by an even greater amount.[5]

Short reaction times to produce the thin layers and fine grains are essential for high J_c, but, at high magnetic fields, J_c becomes limited by T_c, H_{c2}, and grain size. Thus, a compromise must be struck between high T_c and layer thickness to obtain the optimum J(H) characteristics.

Metallurgical Analysis

Specimens were polished, etched, and then anodized in NH$_4$OH to identify different phases by color contrast. The thickness of the Nb$_3$Al layer was determined by optical microscopy. The layer thickness values in Table I are maximum values; different portions of a sample exhibited thinner layers or, at times, no layer. The location of the Nb$_3$Al or (Nb-1% Zr)$_3$Al layer was verified by electron-microprobe analysis. Layer growth in all cases was diffusion controlled ($d \sim t^{1/2}$), and the measured thicknesses agreed closely with those calculated from diffusion data.[6] Typical Nb$_3$Al wires are shown in Fig. 1. In multifilamentary wires, the entire aluminum matrix was reacted. Thus, a practical conductor would require addition of a supplemental stabilizer after the high-temperature diffusion step. The Nb outer jacket would prevent interaction between the stabilizer and composite during the ordering treatment.

The thickness of the Nb$_3$Al layer was influenced by the addition of zirconium as well as the reaction time and temperature. The (Nb-1% Zr)$_3$Al layers were consistently a factor of $\sim\sqrt{2}$ thicker than the Nb$_3$Al layers fabricated under similar conditions (e.g., J7-3 and -4). The effective diffusion constant, D, in Nb$_3$Al is apparently doubled. Zr, which diffuses rapidly in Nb, enhances the Nb self-diffusion[7] and may analogously enhance diffusion in Nb$_3$Al. The presence of carbon was not a factor in the growth of Nb$_3$Al layers.

Scanning electron microscopy results indicate an average grain size, in thicker layers (d > 1.5 μm), of the order of a few microns with a minimum size of $\sim$0.6 μm. Coarse precipitates, suspected to be Zr carbides, were observed at the Nb$_3$Al grain boundaries in Nb-1% Zr samples doped with C$_2$H$_4$.

Critical Currents

$J_c(H)$ was measured in transverse magnetic fields by standard four-point probe techniques, and the results are displayed in Fig. 2. Significant improvement in $J_c(H)$ required a Nb$_3$Al layer thickness of <1 μm.

The dependence of J_c on layer thickness d can be expressed as $J_c(d) \sim J_o e^{-nd}$, where J_o is the extrapolated zero-thickness value of $J_c(d)$. In multifilamentary Nb$_3$Al, $n \sim 0.5$ for d < 1.5 μm and $n \sim 0$ for $d \sim 1.5$ μm. (Nb-1% Zr)$_3$Al layers exhibit $n \sim 0.7$ for all d. J_o, inversely related to the nucleating grain size,[8] is larger for composites with thin Nb$_3$Al layers than for (Nb-1% Zr)$_3$Al layers. This suggests that the presence of Zr in Nb may inhibit nucleation of Nb$_3$Al grains. Consistent with the lower J_o, the larger value of n for (Nb-1% Zr)$_3$Al layers implies a higher growth rate, as observed, and larger grain size than Nb$_3$Al layers grown under identical time and temperature conditions and ZrC precipitates are not pinning the grain boundaries.

Except for samples 5A and B, the pinning force, $F_p(H)$, decreases as H increases, and at 2.0 T the average value is <5 x 10^7 dynes/cm^3. This behavior is suggestive of weak pinning by (a) large grains (>1 μm), (b) a dispersion of carbides, or (c) the presence of degraded (low H_{c2}) Nb$_3$Al. However, samples 5A and B, with a lower T_c, have $F_p(H)$ $\sim$7 x 10^8 dynes/cm^2 at 7 T and a broad maximum at 6.5 T ($\sim$0.25 H/H_{c2} for T_c = 16.5 K). Also, the behavior of $F_p(H)$ with d or, qualitatively, grain size is consistent with results found for grain size versus F_p in Nb$_3$Sn.[9]

TABLE I
Properties of Some Nb$_3$Al Superconductors

Sample	Material	Reaction Temperature, °C	Reaction Time, s	Atmosphere	Nb$_3$Al Thickness, μm	T_c Midpoint, °K	F_p x 10^7 dynes/cm^3 at 2 T
1A	Multifilament	1900	180	Vacuum	9.4	18.2	5
J2	Multifilament	1830	10	Vacuum	<1.5	18.1	7
5A	Multifilament	1800	5	Vacuum	0.5	16.5	30
5B	Multifilament	1800	5	Vacuum	0.7	16.5	28
J7-3	Nb	1900	10	Ar + C$_2$H$_4$	2	17.9	5.5
J7-4	Nb-1% Zr	1900	10	Ar + C$_2$H$_4$	3	17.6	1
J8-2	Nb-1% Zr	1900	5	Ar	1.5	17.4	4.3
J9-2	Nb-1% Zr	1900	10	Ar	2.5	-	1.5

The presence of carbides at the grain boundaries in (Nb-1% Zr)$_3$Al does not, at the concentration of C_2H_4 employed, affect J_c. However, our results agree with those of Müller[2] for 0.5% C_2H_4, and perhaps increased amounts may be beneficial for flux pinning if the carbides can be prevented from coarsening.


(a) (b)

Fig. 1. (a) Micrograph of J7-3 showing 2 µm diffusion layer of Nb_3Al (arrow), 500X. (b) Sample J2 showing completely reacted aluminum matrix (Nb_2Al-$NbAl_3$ eutectic), 1000X.

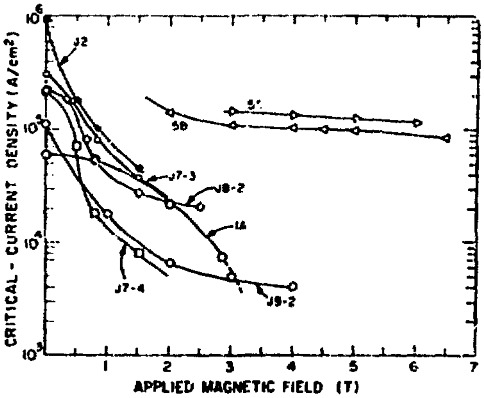

Fig. 2. Variation of the critical-current density at 4.2°K with applied transverse yield for the samples listed in Table I.

IV. CONCLUSIONS

We have fabricated high-quality Nb_3Al multifilament superconducting wire with some of the highest J_c and F_p values reported to date. The Nb_3Al grain size has been found to be the deminate factor controlling $J_c(H)$, however the grain size has not yet been sufficiently refined to produce acceptable current densities at high fields. Carbides have been found to be ineffective as grain boundary and flux pinners. Zr additions are detrimental at high reaction temperatures because they accelerate Nb_3Al layer growth, but this same property may be beneficial for lower-temperature reactions.

ACKNOWLEDGMENTS

The author would like to thank B. P. Strauss and M. Price of the Fermi National Accelerator Laboratory for their assistance and hospitality during measurements of $J_c(H)$.

REFERENCES

1. T. W. Eagar and R. M. Rose, IEEE Transactions on Magnetics, MAG-11, No. 2, 214, 1975.
2. A. Müller, J. Less-Common Metals, <u>42</u>, 29, 1975.
3. J. W. Hafstrom and H. R. Thresh, J. Poly. Science: Polymer Symposia, to be published (1976).
4. F. J. Cadieu, J. Low Temp. Physics, 3, 393, 1970.
5. P. J. Martin, A. M. Campbell and J. E. Evetts, J. Mat. Science, 10, 498, 1975.
6. G. Slama and A. Vignes, J. Less-Common Metals, 29, 189, 1972.
7. S. Ro[illegible], Private Communication.
8. M. Suenaga, T. S. Luhman and W. B. Sampson, J. Appl Phys., 45, 4049, 1974.
9. R. M. Scanlon, W. A. Fietz and E. F. Koch, J. Appl. Phys., 46, 2244, 1975.