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SUPERCONDUCTING PROPERTIES OF A POWDER ROLLED COMPOSITE TAPE CONTAINING Nb_3Sn FILAMENTS

M. R. Pickus,* K. Hemachalam** and B. N. P. Babu***

ABSTRACT

The morphological control and superconducting properties of a composite tape containing Nb_3Sn filaments made by a new powder metallurgy process are reported. Critical temperatures were in the range from 18.1 to 18.5°K. Through procedural improvements overall current densities up to 7×10^4 amps/cm^2 in a pulsed field of 100 kG were realized.

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I. INTRODUCTION

In a recent publication[1] a procedure was described for producing by powder metallurgy techniques a superconducting niobium-tin tape with a controlled morphology. Elemental niobium powder was compacted by powder rolling, and sintered under conditions that produced a ductile tape containing a definite volume fraction of interconnected pores. The pores were filled with tin by immersing the sintered tape in a molten tin bath. Rolling the infiltrated tape (at room temperature) to a reduction in thickness of 75 to 85% established the desired morphology. The deformation caused a pronounced elongation of the tin and resulted in a composite consisting of thin filaments of tin arrayed in a niobium matrix. A thermal treatment for approximately 3 minutes at 950-1000°C converted the material into a superconducting composite in which thin filaments of the brittle Nb_3Sn phase are dispersed in a ductile niobium matrix. Figure 1(a) shows the tape after infiltration at 650°C, and Fig. 2(a), after the normal thermo-mechanical treatment.

It is the purpose of this communication to report on the superconducting properties of the tape and to discuss some improvements that have been made in the fabrication procedure. Mention was made in the report previously referred to that at severe reductions in thickness tin was squeezed out to the surface. The loss of tin resulted in a significantly smaller volume fraction of Nb_3Sn than would have been

anticipated from the volume fraction of tin in the infiltrated tape. This of course results in a proportionate loss of current carrying capacity.

II. EXPERIMENTAL PROCEDURES

A. Prevention of Tin Loss

Several methods were devised for the purpose of retaining as much of the infiltrated tin as possible during the cold rolling operation. In considering their respective merits, an important criterion, in addition to effectiveness, was the relative ease of carrying out the procedure. For example, cladding the tape with a layer of niobium prior to rolling provided very good tin retention. However, with the limited facilities available the cladding was a very tedious operation.

Data will be presented for tapes prepared by two different procedural modifications which were easily carried out and which gave increased volume fractions of Nb_3Sn. In one modification the infiltrated tape was rolled cryogenically. Figure 2(b) shows the microstructure of a tape that was thermally treated to form Nb_3Sn after having been rolled at a temperature of -72°C. The volume fraction of Nb_3Sn may be compared with that shown in Fig. 2(a), a micrograph representative of "normal" processing. In a second modification, the tin was hardened by a controlled inclusion of intermediate phases. This method for hardening the tin to prevent squeeze-out losses was the simplest to carry out. Reference to Fig. 3, an alloy diagram[2] for the niobium-tin system, shows that after infiltrating at the usual temperature of 650°C, it is thermodynamically possible to have niobium, Nb_3Sn, Nb_6Sn_5, $NbSn_2$ and tin all present in the as infiltrated tape. Nevertheless the reaction kinetics at this temperature for the short immersion times employed (one minute) are such that virtually none of the intermediate

phases are present, as may be seen in Fig. 1(a). If the infiltrating temperature is increased to 850°C, however, there is a marked change in the reaction kinetics. Figure 1(b) shows that tape infiltrated at this temperature for one-half minute contains a significant amount of intermediate phases, predominantly Nb_6Sn_5 which is readily distinguished under the microscope by the characteristic reddish brown color imparted by anodic etching. It is anticipated that proper control of these phase reactions could lead to the maximum volume fraction of Nb_3Sn realizable from the volume fraction of infiltrated tin. A tape that had been infiltrated at 850°C, rolled at room temperature and thermally treated at 970°C is shown in Fig. 2(c).

B. Critical Temperature Measurements[3]

The four point probe employed accommodated two samples and two germanium resistance thermometers calibrated to within ± 0.1°K over the temperature range from 4.2 to 40°K. In order to minimize temperature differences between test components--samples and thermometers--the two samples were mounted on one side of a copper block which constituted one end of the probe, and the two germanium thermometers were mounted on the other side. The block, itself, was enclosed within a cylindrical copper cap.

A temperature gradient, existing in the neck portion of a long-neck dewar when the liquid helium level was maintained just below the neck, provided the means for obtaining different test temperatures. The voltages developed by passing constant currents through the sample and thermometer--100 and 10 microamperes respectively--were amplified and recorded simultaneously on an X-Y recorder. The width of the transition

between the superconducting and normal states (as shown by the vertical bars in Fig. 4) was taken as the temperature difference corresponding to 10% and 90% of the voltage signal recorded for the normal state.

C. Critical Current Measurements

A pulsed magnet,[4] having a pulse rise time (the time between the zero point and the quarter sine wave point) of approximately 8 milliseconds, and capable of producing field strengths in excess of 200 kG, was used to determine the critical current-magnetic field relationship at 4.2°K. In order to have the pulse data correlate well with steady state data, the time derivative of field strength should be as nearly zero as possible. This condition was achieved by adjusting the magnet current so that the critical field (H_{C_2}) for a given sample current occurred at or very close to the peak value of the pulsed field. Babu[3] and Garrett[4] each made comparative tests using a 90 kG D.C. magnet, and found good agreement with their pulsed data determined in this fashion. To prevent overheating of the test samples, after the transition to the normal state had occurred, the current through the sample was automatically cut off just beyond the peak of the field pulse.

The orientation of transport current in the sample with respect to the magnetic field, as well as the main features of the pulsed magnet apparatus, are shown schematically in Fig. 5.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Critical Temperature (T_C)

The observed relationship between critical temperature and reaction temperature is shown in Fig. 4. Values for T_C ranged generally from 18.1 to 18.5°K. It has been reported[5] that such high T_C values can be obtained only as a result of a special ordering treatment at optimum temperatures between 950 and 1000°C. The present work, in which these values were observed after very short heat treatments (1-5 minutes) suggests that if ordering is necessary, it must occur rapidly. It was also found that for heating times from a few minutes to one hour T_C remained constant from 900°C to 1100°C, and then reached a maximum value at 1200°C that persisted to 1300°C. Interestingly, A. I. Golovashkin[6] of the P. N. Lebedev Physics Institute of Moscow reported a similar maximum at 1200°C in their work on co-evaporated thin films.

The value of T_C was found to be insensitive to the degree of plastic deformation prior to the normal thermal treatment. However, cold working did facilitate the formation of Nb_3Sn at lower temperatures such as 800-850°C. Whereas samples thermally treated in this range immediately after infiltration showed no indication of containing Nb_3Sn, samples reduced 50, 75, 85 and 95% in thickness prior to the thermal treatment exhibited fairly high T_C values of 17.6 to 17.9°K. This confirms the findings of Charlesworth, et al.[2]

An interesting observation was made with respect to the influence of stoichiometry on the value of T_C for these tapes. Microprobe analysis confirmed the expectation from the phase diagram (Fig. 3) that samples thermally treated to contain in equilibrium only the two phases, niobium

and Nb_3Sn, would exhibit no composition gradient in the Nb_3Sn. The composition was estimated to be between 17 and 18 atomic per cent tin corresponding to the stoichiometry referred to as the Nb_4Sn phase in the earlier literature.[7] In samples thermally treated for retention of some unreached tin, on the other hand, there was indeed found the expected gradation in the composition of Nb_3Sn, from about 18 to 26 atomic per cent tin. No significant difference in T_c was found for the two thermal treatments. This does not agree with some reports[8,9] to the effect that niobium rich Nb_3Sn has a low T_c, but confirms the results of Reed, et al.[10] and Courtney, et al.[11]

B. Current Carrying Capacity in Pulsed Fields

The overall current density values shown in Fig. 6 were determined on the basis of the entire cross section of the tape, exclusive of the surface coating of tin. Reporting the data in this manner circumvents the uncertainties involved in the determination of the Nb_3Sn volume fraction which is required for calculating J_c (the critical current density of the superconducting phase). These uncertainties arise from the complex filamentary morphology of the composite tape and from the presence of a small residue of unreacted tin within the Nb_3Sn filaments. Furthermore, since it depends on both the value of J_c and the volume fraction of Nb_3Sn, the overall current density provides a meaningful indication of the merit of the tape as a practical superconductor.

Curves (a), (b) and (c) of Fig. 6 were obtained from tapes whose photomicrographs are shown in Fig. 2(a), (b) and (c) respectively. It was anticipated that the only significant effect of the different thermo-mechanical histories would be a difference in the volume fraction

of Nb_3Sn. This was in fact found to be the case. Approximate determinations of the volume fractions gave values of 30% for Fig. 2(a), 40% for Fig. 2(b) and 50% for Fig. 2(c). The ratios of current densities for a given field taken from curves (a), (b) and (c) of Fig. 6 are found to agree very well with the corresponding ratios of the volume fraction of Nb_3Sn.

Further increases of appreciable magnitude in the volume fraction of Nb_3Sn are considered unlikely. However, significant enhancement of the intrinsic current carrying capacity of the Nb_3Sn filaments (J_c) together with a marked decrease in the slope of the current density vs magnetic field curve at high field strengths have already been indicated in preliminary experiments with zirconium doping. This potentiality will be investigated more extensively and reported at a later time.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Fig. 1. Porous niobium tape infiltrated with tin. a) Infiltrated at 650°C. b) Infiltrated at 850°C. Phase designations: Niobium, 1; tin, 3; Nb_6Sn_5, 4.

Fig. 2. Thermo-mechanically processed tape. a) Infiltrated at 650°C, rolled at room temperature and thermally treated at 970°C. b) Infiltrated at 650°C, rolled at -72°C and thermally treated at 970°C. c) Infiltrated at 850°C, rolled at room temperature and thermally treated at 970°C. Phase designations: Niobium, 1; Nb_3Sn, 2; unreacted tin, 3.

Fig. 3. Alloy diagram[2] for the niobium-tin system.

Fig. 4. Relationship between critical temperature and thermal treatment for cold worked tapes. The vertical bars indicate the width of the transition from the superconducting to the normal states.

Fig. 5. Schematic representation of pulsed field apparatus for critical current measurements. Sample width is in plane of paper.

Fig. 6. Pulsed field dependence of current carrying capacity. Curves (a), (b) and (c) correspond to the photomicrographs (a), (b) and (c) of Fig. 2.

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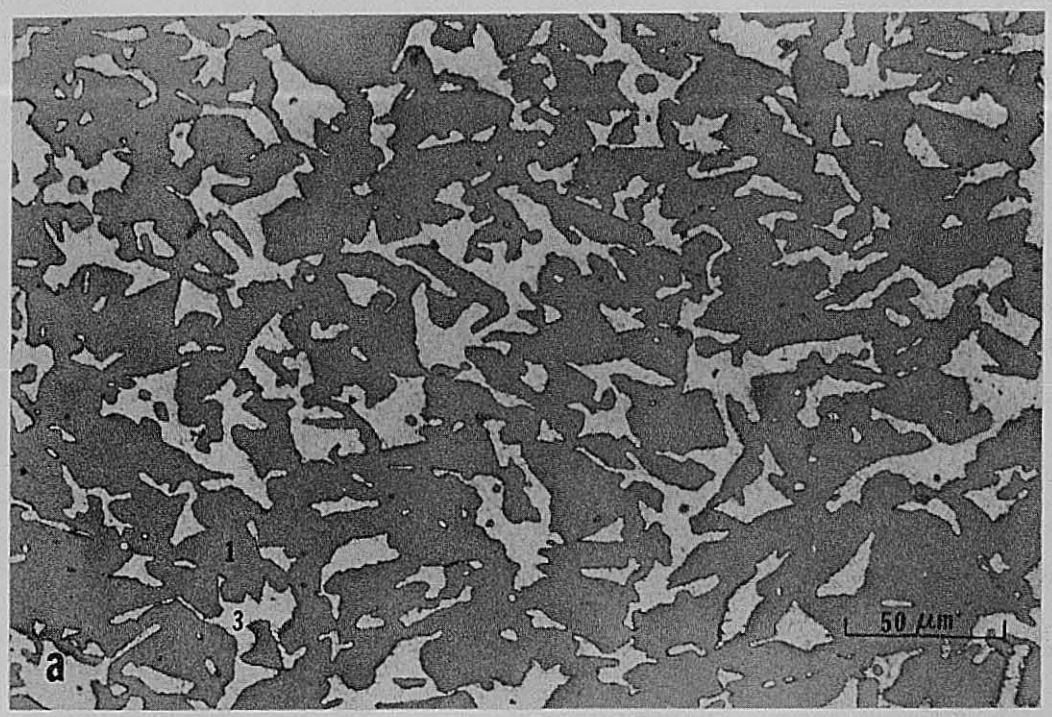

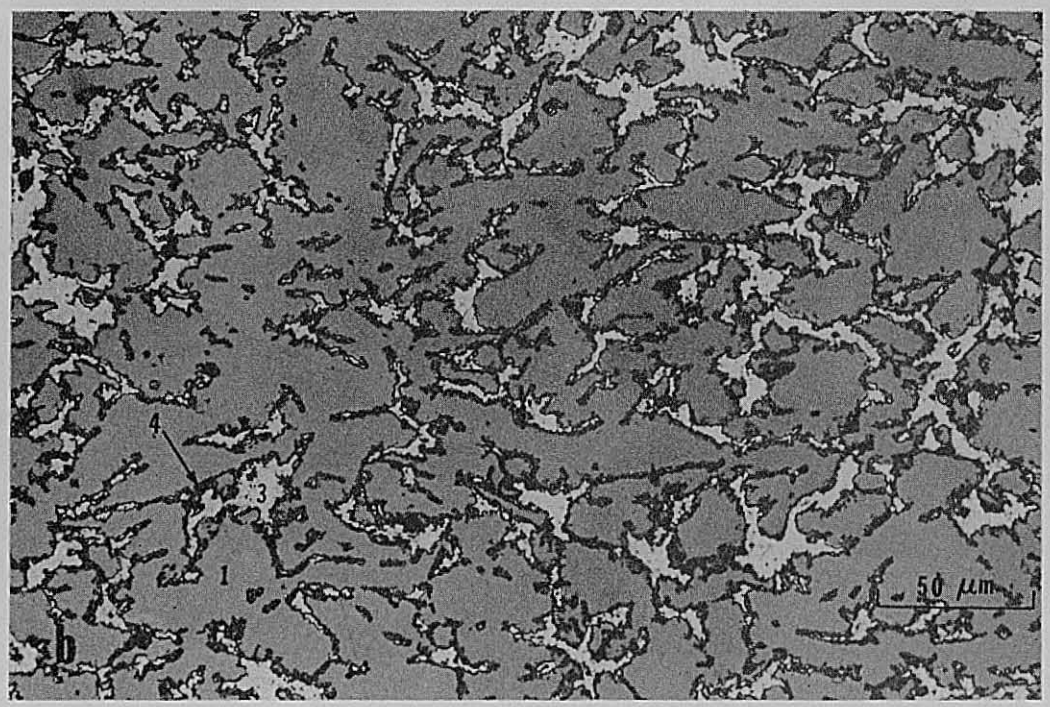

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Fig. 1

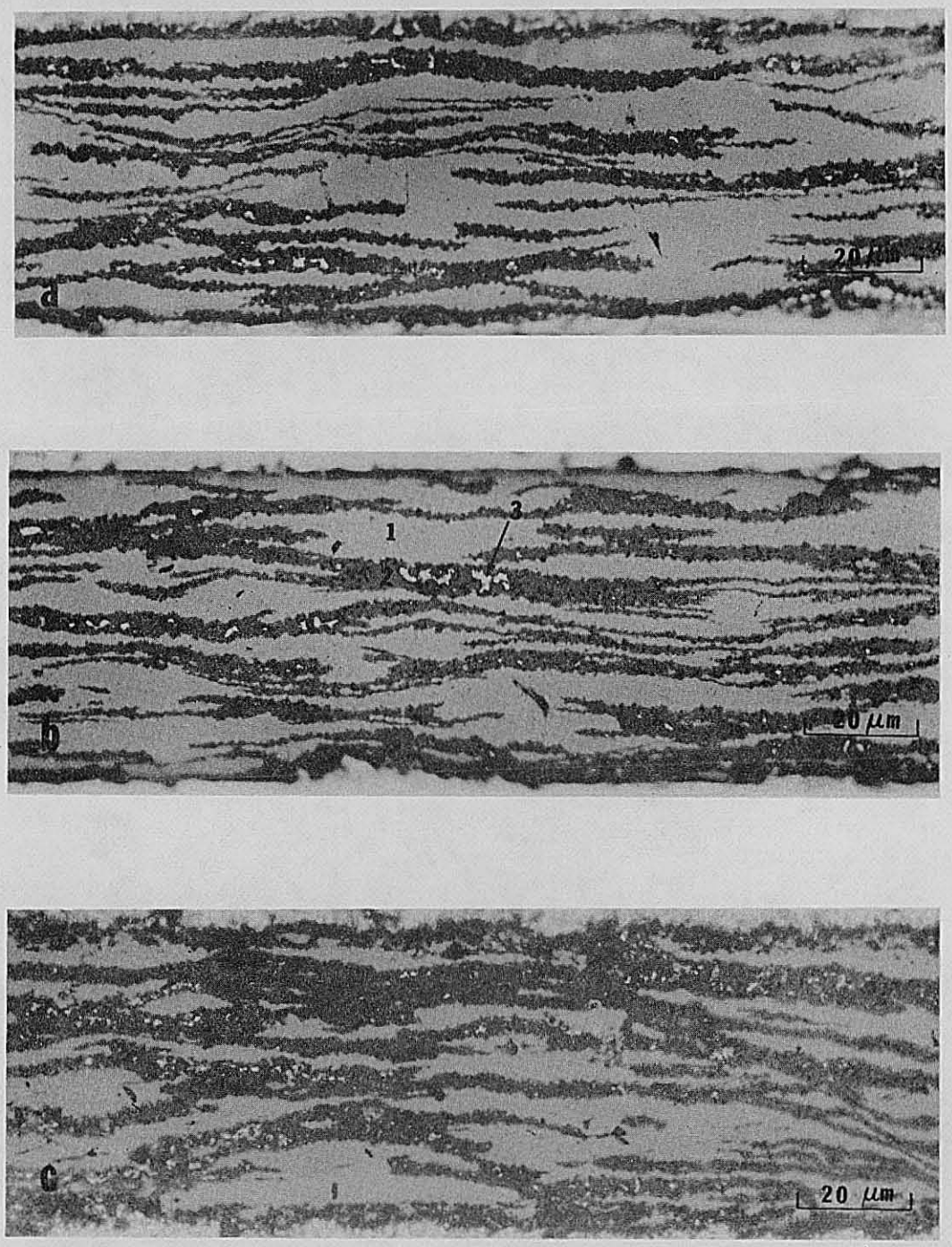

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Fig. 2

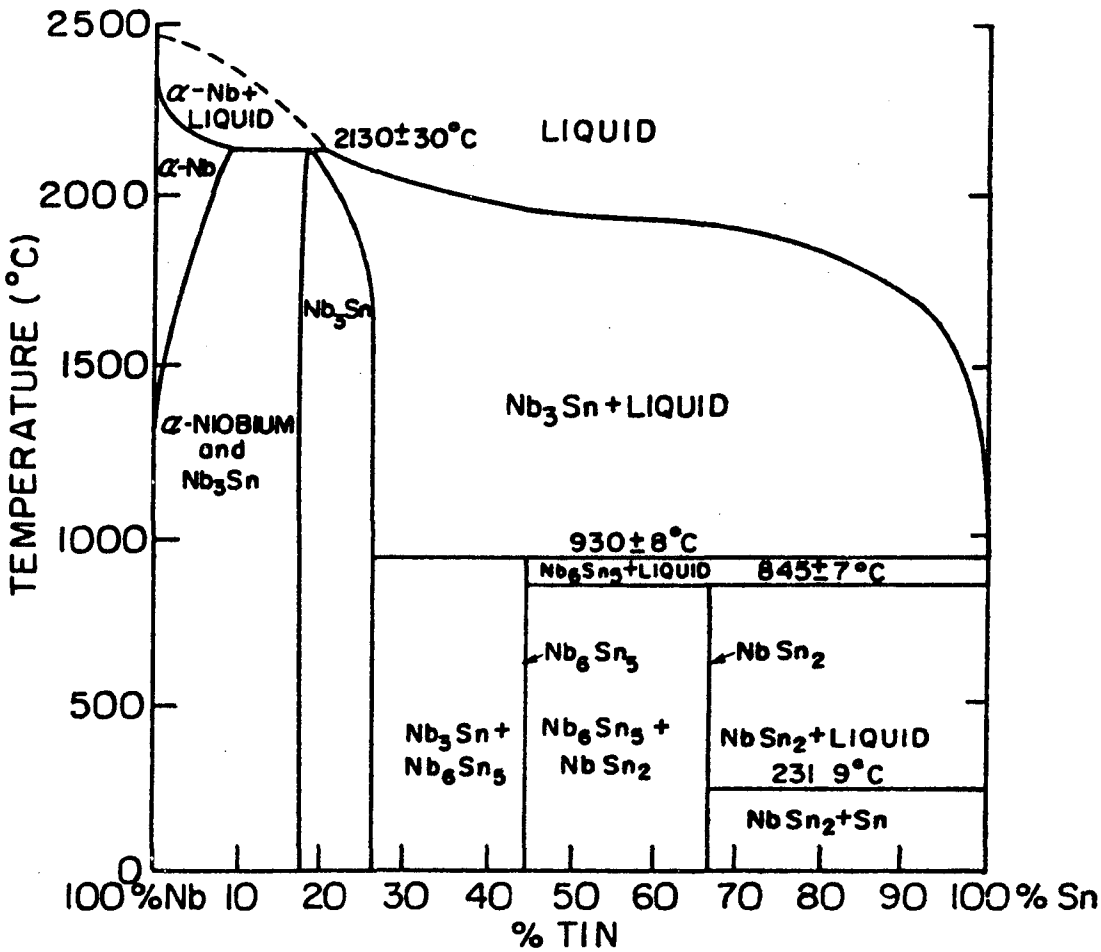

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Fig. 3

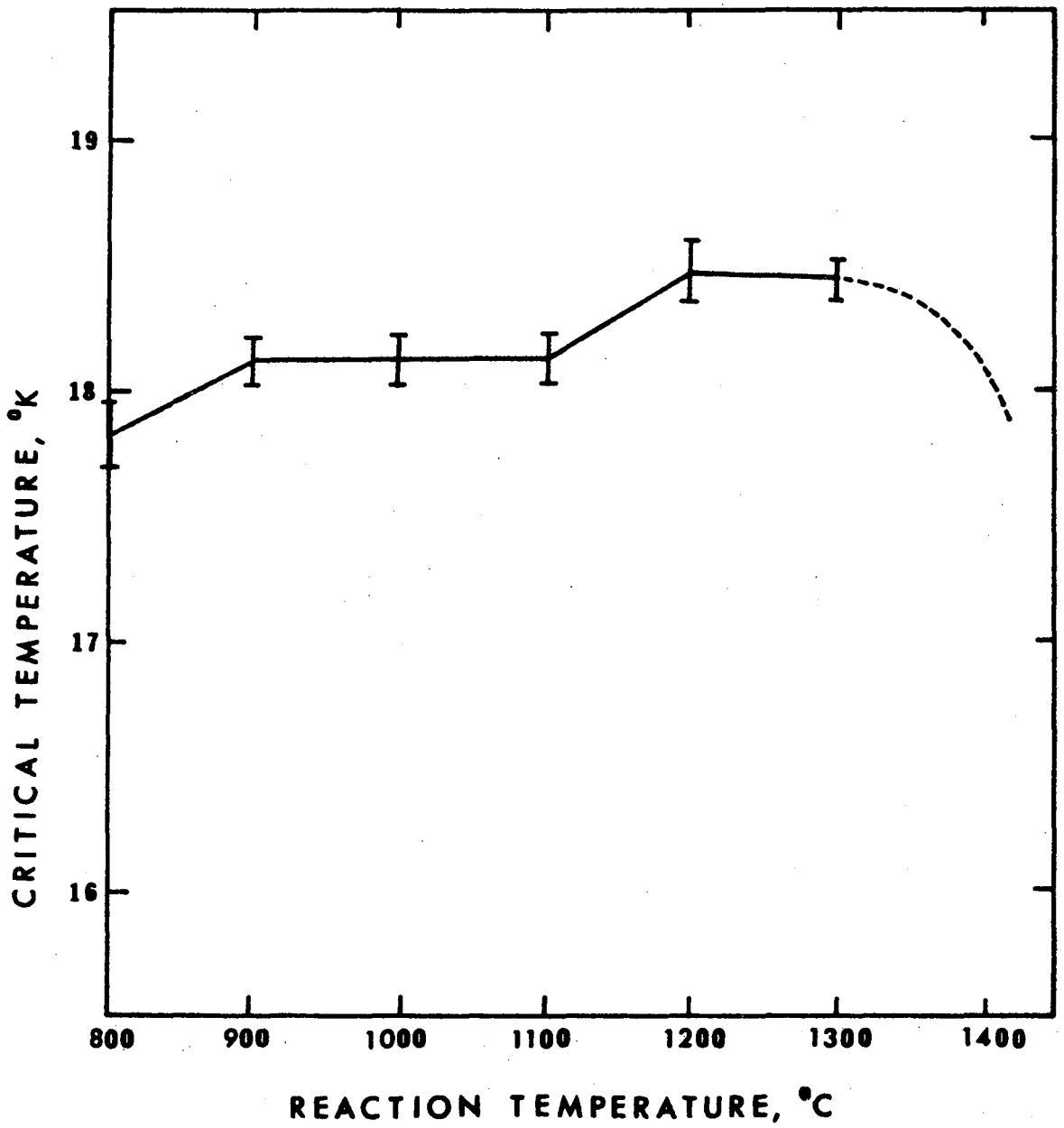

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Fig. 4

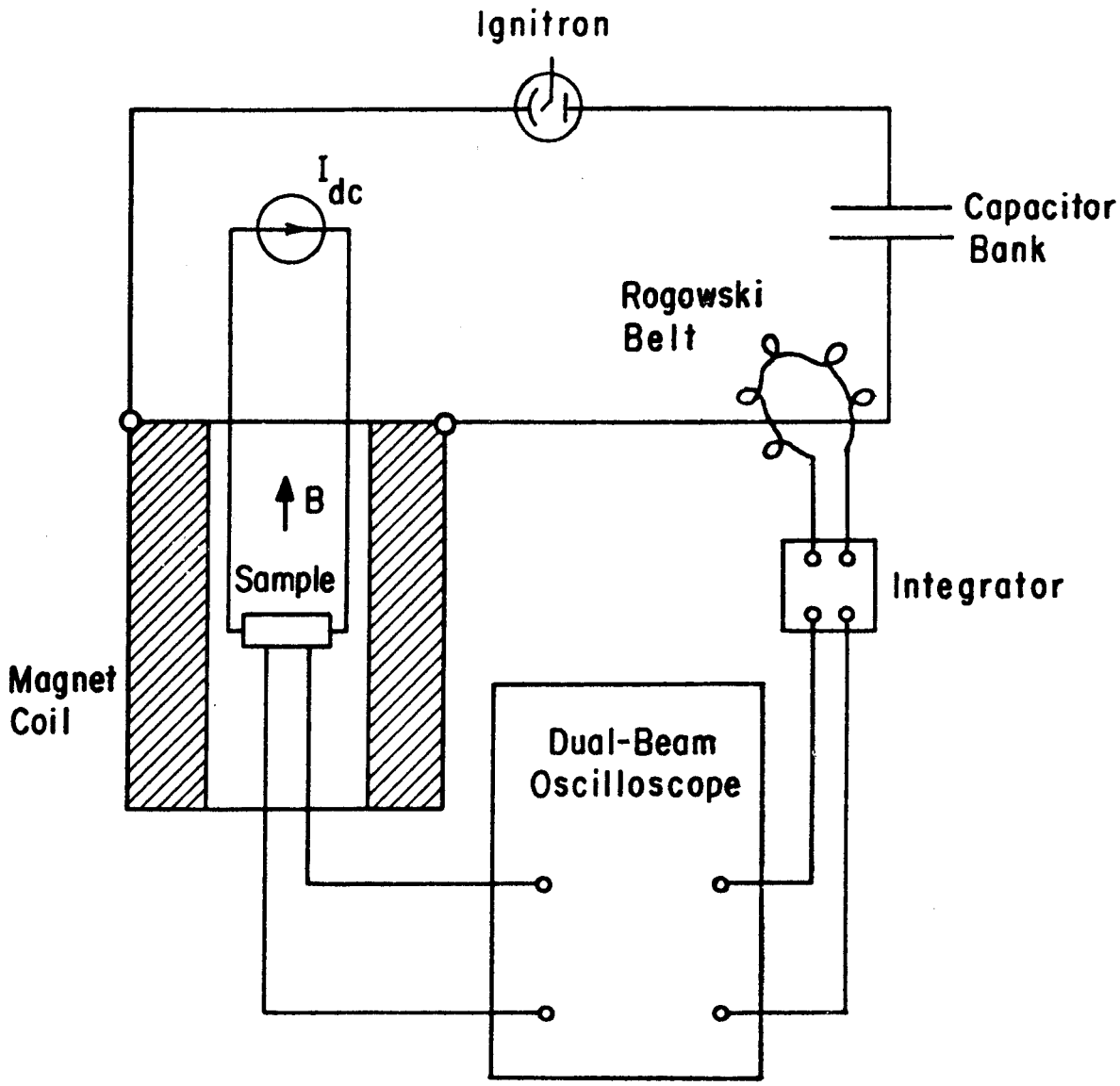

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Fig. 5

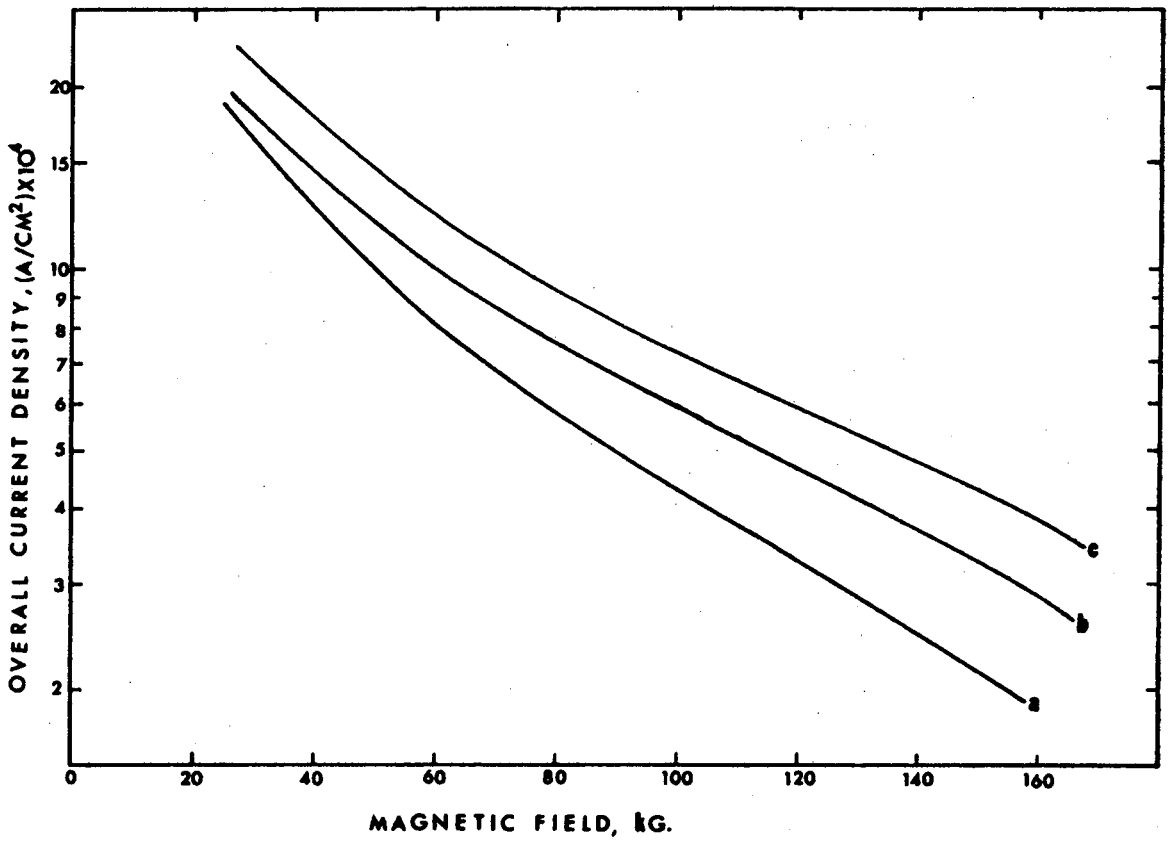

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Fig. 6

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