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Indigenous development of niobium-based superconducting materials

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Abstract. A programme jointly launched by Bhabha Atomic Research Centre, Trombay and Reactor Research Centre, Kalpakkam to develop indigenously, niobium titanium alloys for superconducting magnets is described. Results of short sample tests on specimens with different treatment are presented. Future plans are also outlined.

Superconducting materials on account of their ability to support loss-less currents have been exploited in the past for producing magnetic fields of large strengths, particularly for scientific research. During the last decade, the technological applications in this field have been so immense that superconducting magnets are no longer regarded as mere laboratory gadgets. Powerful superconducting magnets have been employed in high energy particle accelerators, in fusion research, in MHD power generation programmes and in levitated transportation projects. Superconducting materials are also expected to be used in low loss transmission of large blocks of power, and massive research programmes are in progress in many countries.

The two most important superconducting materials that have been in use the world over are both niobium-based alloys: niobium-titanium and niobium-tin. Both these materials have reasonably high transition temperatures (T_c)—with respect to the temperature of liquid helium in which environment the magnets usually operate—and can support high current densities in the superconducting state. While niobium-titanium has favourable mechanical properties with respect to formability, niobium-tin is brittle and requires special methods of wire fabrication. The critical current (J_c)—the maximum current that the superconductor can support—is in general influenced by the alloy composition, cold work and the heat treatment that the material has undergone, and it is also sensitive to grain size and impurity content. On the other hand, the transition temperature is rather insensitive to these parameters in the case of the niobium-titanium solid solution, while it is highly influenced by the stoichiometry and the degree of long-range ordering in the case of the niobium-tin intermetallic compound.

Indigenous development of superconducting materials calls for strong and well co-ordinated research and development efforts in diverse disciplines—first to establish reliably the influence of the mechanical, thermal and metallurgical parameters on the superconducting properties, and then to standardise fabrication techniques of long lengths of wires in a form that can be directly used to wind magnets. Production and purification of the component metals, synthesis of the alloys, formation into wires of suitable geometry by the processes of forging, extrusion, rolling and drawing, heat-treatment, determination of structure by electron microscopy and characterisation of short samples for evaluation of superconducting properties—all these are essential components in the comprehensive development programme.

With a view to building up national expertise in superconducting materials technology, a programme was initiated a few years ago jointly between the Bhabha Atomic Research Centre (Trombay) and the Reactor Research Centre (Kalpakkam). The programme sought to utilise the metallurgical and cryogenic skills already available in the various wings of the Department of Atomic Energy towards preparing, in the first instance, wires for superconducting magnets. The four refractory and reactive metals, viz., niobium, zirconium, titanium and vanadium are among the most proven basic materials for superconducting materials technology, and these are also well known in their large scale use in nuclear, chemical, aerospace and other allied branches of engineering. As it stands to-day, there exists in the country a fairly well-established technical base and expertise in the production and processing of all these special metals and their alloys. The metal zirconium is being produced for nuclear applications in tonnage quantities at the Nuclear Fuel Complex, Hyderabad. A pilot plant for titanium production is also currently operating at the same site. Iodide refining to purify sponge titanium and zirconium has been standardised. Processes involving aluminothermic reduction followed by electron beam melting/molten salt electro-refining have been developed at Trombay for the production of niobium and vanadium metals in kilogram lots. Facilities for production, melting and purification to produce superconducting alloy compositions from these metals in their final purities in at least two or three kilogram lots are available, and can be stepped up to keep pace with demand.

In the superconductor development programme at Trombay, the major effort so far has been on the Nb–Ti system. Starting with high purity niobium and titanium, the fabrication technology for the production of oxygen-free high conductivity (OFHC) copper clad single core Nb–Ti wire has been investigated at the Metallurgy Division, BARC. The flow sheet involves the preparation of the alloy melt by electron beam melting, cold reduction of the alloy cast to wire rod (4 mm dia), insertion of the wire rod in an OFHC copper slug, co-reduction and co-drawing of copper clad Nb–Ti to a final diameter of 0·3 mm. Wires of lengths upto 50 m have been produced adopting this procedure. The wire has been finally given heat-treatments at temperatures in the range of 300–400° C for durations from 2 to 4 hr.

Superconducting properties of the fabricated wire are evaluated by measuring both J_c and T_c values of representative short samples (2 cm in length) from a particular batch. The J_c value is evaluated at a temperature of 4·2 K under an external magnetic field upto 5 T. The set up used for the purpose (figure 1)—at the Reactor Research Centre, Kalpakkam—consists of a 30 mm bore superconducting solenoid capable of producing a maximum field of 5 T at a current of 50 amp. The magnet is powered by a current regulated supply with a regulation better than 0·5%. A protective device against quenching of the super-

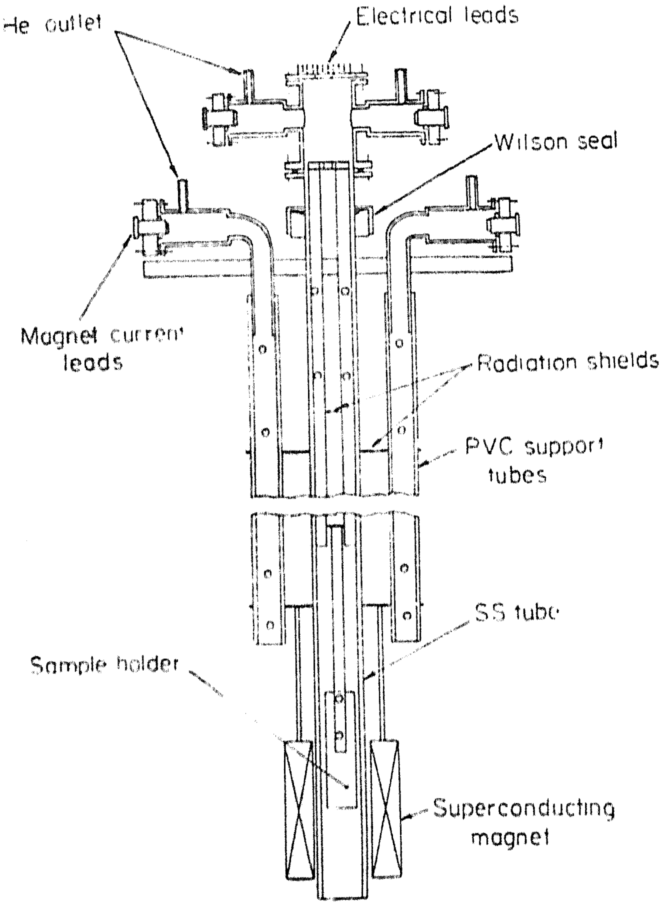

Figure 1. Experimental assembly for evaluation of superconducting properties.

conducting magnet is also incorporated in this system. The test specimen (wire or strip) is held in the centre of the bore of the magnet in such a way that the direction of the current in the sample is transverse to that of the field produced by the magnet. A maximum current of 100 amp could be passed in the specimen with separate power supply leads. The sample assembly with its high current leads are contained inside a 25 mm dia stainless steel tube which in turn is inserted in the magnet bore placed in a glass liquid helium dewar. The transition to normal state is detected resistively, and a drop of 50 μV across the sample is selected as the criterion. Results of short sample studies carried out in this set-up, with Nb–50% Ti alloys given different treatments, are shown in figure 2. It can be seen that severe cold working improves the J_c value by a factor close to 10. Heat treatment of the material at the final stage at 450° C also enhances J_c by an additional factor of 10.

The same set-up with a minor modification could be used for the measurement of transition temperature T_c. The sample in this case is fastened to a copper block whose height could be varied with respect to the level of liquid helium in the dewar. The temperature of the block is sensed by an Allen-Bradley carbon resistor and is controlled by a proportional integrating type temperature controller which actuates a heater. The temperature control is obtained against the enthalpy of vapour surrounding the copper block. Overall temperature reliability of better

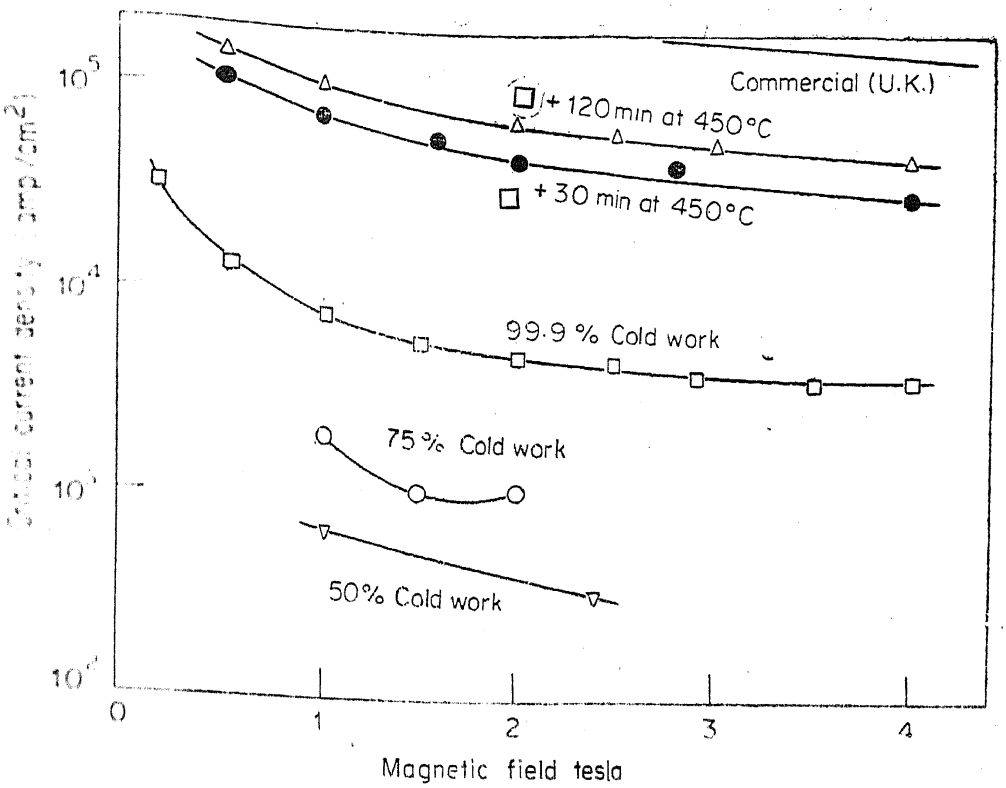

Figure 2. Performance characteristics of Nb–Ti wires given different metallurgical treatments.

than 5 mK has been obtained in this set-up, below 20 K. The superconducting transition is sensed by the four probe resistive method.

A practical superconductor should have a high J_c value and this being a structure sensitive property, all variables of the manufacturing process should be so chosen in order that a suitable microstructure develops. Generally heavy cold reduction ($>$ 90%) that introduces high dislocation density is conducive to obtaining higher J_c values. Pinning of magnetic flux penetrating the superconductor by these line defects is responsible for higher J_c. Final heat-treatment at ~ 450° C tha causes precipitation of finely dispersed Ti-rich α phase enhances flux pinning further and consequently increases J_c value by a factor of 10. Transmission electron microscopy (TEM) with foil alloy samples of Nb–Ti quenched from 1000° C has shown the retention of the precipitates β phase, and ageing of this sample at 400–500° C gives rise to α in the β matrix. In addition, a mottled contrast has been observed in the aged specimen suggesting the occurrence of a phase transition through a spinodal process.

The studies carried out so far have given an insight into structure-property correlation in Nb–Ti superconducting wires. While the experiments hitherto have been mostly with single-core wire, the conclusions can be extrapolated to the fabrication of multifilamentary composites. More recently the work has been extended to investigate also the preparation of Nb_3Sn superconductors by the bronze route.

To sum up, it can be said that considerable progress has been made in the fabrication technology, metallurgical characterisation and property evaluation of Nb–Ti superconducting alloys. It is proposed to continue this development programme upto the stage of producing kilometre length wires required for high field magnets. This appears entirely feasible with the facilities available within the Department of Atomic Energy.

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