# Some reminiscences of two decades of research on high-field superconductors

I joined the Metallurgy Division at Harwell in October 1960, straight from my undergraduate years at Cambridge. At that time there was no interest in superconducting materials and I was temporarily put to work on the very new Cameca Electron Probe Microanayser.

However, in 1961 Kunzler, Buehler, Hsu and Wernick revealed their finding that the intermetallic compound Nb3Sn would carry large supercurrents in high magnetic fields at liquid helium temperatures. This caused a good deal of excitement in the local scientific community (Harwell and its two spin-offs, the Culham Laboratory (fusion research) and the Rutherford Laboratory (high energy physics). The Metallurgy Division decided to start a small program of research on these materials in Mike Poole's group and I was assigned to work with Peter Madsen, initially on establishing the constitution diagram of Niobium Tin alloys. Peter had done similar work on uranium alloys but my only qualification was that my Cambridge director of studies, David Shoenberg, who established the concept of the superconducting penetration depth and author of a book on superconductivity had given me an interest in low temperature physics.

Three types of alloy samples were produces, homogeneous alloys by h.f. melting, diffusion samples from solid niobium in contact with liquid tin, and powder compacts made by pressing niobium and tin powders in different concentrations. The samples were heat treated at various temperatures and quenched quickly to room temperature to 'freeze in' the high temperature structures.

The primary method of indentifying the phases produced was optical metallography but the large range in hardness of the phases caused problems in preparation which were eventually solved by our colleague Ian Macphail. The samples were frequently rather porous which made chemical etching problematical, so the primary means of delineating phases was cathodic ion-bombardment etching. The ions sputter away material from some phases more quickly than others, so a step is formed at the phase boundaries, as well as, to a lesser extent, at grain boundaries. The phases could often be identified through small colour differences and by different behaviour under polarised light but much clearer identification could be obtained by anodising the surface with a dilute citric acid solution. Where pure tin was present, it was necessary to adjust the voltage to obtain a standard colour on some pre-identified phase.

The Cameca Micoanalyser proved a godsend in obtaining the chemical analysis of the phases. Some information about the temperatures at which phase changes occur was also obtained by thermal analysis.

The final output of this work was a constitution diagram for the lower-temperature section of niobium-tin alloy system (i.e. not covering the melting temperatures. The work, although completed in the mid 1960s was not published until 1971 in a paper which presented a comparison of our findings with those in other published work and proposed a definitive version of the complete constitution diagram, combining work from all sources.

While this was going on I was taking my first steps into experimental superconductivity by building a rig for measuring superconducting transition temperatures $T_c$, in particular on the intermetallic compounds on the Nb-Sn alloy sytem. At that time, although we had a divisional workshop which could construct small items, there was no engineering effort assigned as part of the project team, meaning we had to design our own equipment and largely build it ourselves. I quickly got pretty good at soldering and brazing copper pipes for vacuum systems but, at one stage, acquired an unenviable reputation for flooding the building in the early hours (when the water pressure always seemed to rise) through neglecting to clip my flexible cooling-water pipes properly.

Stainless steel helium cryostats were unheard of, silvered glass vacuum vessels being still almost universal, with the consequence that most of us had experience of implosion failures producing showers of glass 'shrapnel'. I don't recall anyone ever being injured in this way but it upset the Safety Committee! At some stage during the mid 60s I acquired a metal cryostat which had a thin-wall stainless steel tube for the inner wall of the helium vessel, the outer wall and those for the liquid nitrogen vessel being brass. This was constructed one of the technicians in the Clarendon Laboratory of Oxford University. These men had a useful line in extra-mural contracts at that time but had not yet thought to set up as a specialist low temperature physics equipment company, as was later to happen with Oxford Instruments.

In the early 1960s there was little in the way of electronic instrumentation and what there was was primitive by today's standards. For instance the X-ray detectors on the Cameca had decatron counter tubes to display the intensity.
In my $T_c$ rig, temperatures above 4.2K were measured by thermocouples but I cannot remember how we measured the voltage accurately. For temperatures below 4.2K we could use the vapour pressure of liquid helium as measured by an accurately calibrated aneroid vacuum gauge or a mercury-filled U-tube manometer. A colleague in Electronic Division designed temperature control system for my $T_c$ rig using a light source and photocell detector looking at the meniscus of an oil manometer and controlling the power input to a heater to keep the temperature of my samples constant.

The metal cryostat was designed to contain a new superconducting magnet wound from Nb-Zr alloy wire and producing fields up to 45KOe. With this I was able to start measuring the critical currents of various materials as a function of magnetic field.

In particular Peter Madsen and I studied the effects of cold work and heat-treatment on critical currents of various Nb-Ti alloy wires. This is not the place to review the results in detail but some explanation of our interest is worthwhile. In Type II superconductors, at applied magnetic field greater than the lower critical field $H_{c1}$, magnetic flux penetrates the superconducting material in the form of flux vortices. An applied current exerts a force on these vortices which would move them, with consequent power dissipation, if they were not somehow able to resist the force. The feature of the material which resists movement of the flux vortices is called 'flux pinning' and a treatment which increases the pinning enhances the material's usefulness for, for instance, creating high-field magnets.

Cold work has the effect of introducing dislocations into the material, often in a non-uniform distribution and these dislocation structures seem to have some flux-pinning capability in themselves. Subsequent heat treatment can have a variety of effects, for instance, modifying the distribution of dislocations, migrating impurities to the dislocation, decorating the dislocations with precipitates of a different phase or producing precipitate phase structures not correlated with the dislocation distribution.

In Ti-rich NbTi alloys, precipitates of phase-decomposition products occur and these may in some cases act a flux-pinning centres, but where they are present while the material is being cold-worked, they can increase the density of dislocations produced and so enhance the flux-pinning. Alloys richer in Nb do not show phase-decomposition and do not develop such high dislocation densities as a result of cold-work. In my PhD thesis, I presented detailed studies of Ti-45%Nb alloys in which flux-pinning could be enhanced by suitable heat treatment. I showed that, using the concept of measuring the maximum magnetic force that the flux vortices could resist, as a function of heat-treatment, it was possible to derive activation energies for processes occurring during heat treatment. For low temperature heat treatment, I found good agreement with a model which assumed that interstitial impurities were migrating the boundaries of dislocation cells, while for higher temperature heat treatment, which reduced the pinning force, growth of the dislocation cells appeared to be the mechanism. Although these alloys were not good candidates as the more Ti rich ones for use in magnets, from a scientific viewpoint the work was very satisfying.

Meanwhile we had been reorganised into a new Solid State Division and a new Superconducting Materials Group under Brian Howlett where $Nb_3Sn$ was still, and would remain, our dominant interest. The fundamental problem was how to produce this brittle intermetallic compound in a form suitable for making high-field magnets. Like other groups tackling the same problem, we first thought that thin tapes were the answer and put a good deal of effort into developing production routes which could create long lengths of tape suitable for winding magnets.

By this stage, we had made a case for increased funding of the project and were assigned an engineer, Sid Burnett, to help us build the larger scale equipment needed. I was not very closely involved in this work, except as an authority on how to measure critical currents but I remember one particular incident. Sid had created a sort of reel-to-reel tape processor with a tall vertical furnace through which tin coated niobium tape could be drawn at a whatever speed and temperature was required to optimise the critical current. I was working with Fraser Old, who was much more closely involved than I, and I think we were aiming to produce a long length of tape which would contain sections which had received the whole gamut of different heat treatments for critical current evaluation.

The tape run took a long time and it was late in the night before it was complete and we could examine the tape. The first job was to identify which sections of tape corresponded to which treatment which should have been straightforward as the tape ran over jockey wheels with revolution counters. However, the length of tape we had didn't match the recorded revolutions so it was obvious that the tape had been slipping on the jockey wheels and we had to try to calibrate the tape some other way. By examining every inch of the tape under a binocular microscope, we were eventually able to identify surface features which indicated the boundaries between the different heat-treatment sections. We went home tired but jubilant that we had rescued that expensive length of tape from oblivion in the garbage can!

It also soon became clear that the critical problem in constructing superconducting magnets is ensuring stability against catastrophic quenching caused by small movements of flux vortices rearranging themselves against pinning sites during field ramping. For this purpose, a wire containing many thin filaments of superconductor embedded in a normal conducting matrix of low resistivity, providing dynamic stabilisation, is much more attractive than a tape, as the filaments, if fine enough are adiabatically stable and the matrix can help to damp out propagation of fluctuations to neighbouring filaments. Work along these lines was started in Brian Howlett's group at Harwell in 1969 with the progressive development of the so-called 'bronze-route, method of fabrication using niobium rods embedded in copper-tin bronze, the $Nb_3Sn$ being created by heat-treatment to create a reaction layer between the tin and the niobium. In early 1971, Brian Howlett was tragically killed in a climbing accident and, in the resultant reorganisation the group moved into Chemistry Division with Jim Lee as group leader.

I was involved in this program to the extent of measuring the properties of the material produced but the bulk of the effort went into development of a production line for ever more sophisticated composites. The fabrication route involved drilling a matrix of 37 holes in a cylindrical bronze billet, using a gun drill, inserting niobium rods and then swaging and drawing the material to bring the bronze into firm contact with the niobium and to reduce the overall diameter. The process could then be repeated, one or more times, using the previous stage composites as inserts. Many people worked on this program but Derek Armstrong, who toured the country acquiring second-hand machine tools to build up the industrial-scale fabrication shop we needed and threw himself with enthusiasm into developing the fabrication route.

All along this work had been in collaboration with a team at the neighbouring Rutherford Laboratory interested in producing practical solenoids with possible particle accelerator applications in mind. Again there were several people involved but our liaison was chiefly through David Larbalestier and Chris Scott. A joint paper in 1974 describes composites with filament counts up to 42,439 and including regions of pure copper protected by a diffusion barrier to add extra stabilisation. Another paper of the same date describes the successful performance of several small solenoids made from our bronze-route material by winding the material as-fabricated and then heat-treating the whole coil to produce the $Nb_3Sn$.

Chemistry Division had, for some years, had an exchange program with Oak Ridge National Laboratory (ORNL) and, following a period in which Carl Koch worked with us at Harwell, I was fortunate to be able to spend rather more than a year at ORNL in 1973-74, working with Carl and with Don Kroeger.

In those days, ocean liners were still a means of travel rather than a place to have a holiday, so we travelled both ways on the Queen Elizabeth II, with a car in the hold. We arrived in Oak Ridge, Tennessee, just before Labor Day 1973.

Karl and Don had already started a project for comparing various ways of measuring flux gradients in type II superconductors and I had been impressed by a technique developed by Campbell and Evetts at Cambridge University, so I took on the task of adding the Campbell method to their comparative study.

This was my first visit to the USA and also a sort of sabbatical, after 13 years at Harwell, so it was a very enjoyable time with freedom to work on whatever interested me, and to attend conferences and visit other laboratories. In the early summer if 1974, my wife and I embarked on a 6000 mile trip to the West Coast, a mix of lab visits and camping in national parks.

In summary the comparative flux-pinning study showed good agreement between several methods of measurement in some materials but in others the methods seemed to be affected to differing extents by surface properties of the materials.

In the summer of 1974 David Griffiths, from Oregon State University, Corvallis, joined us for a short project studying ac losses in type II superconductors. This was the start of an interest for me which I pursued further on my return to Harwell.

The final stage of my period in the USA was attendance at the 1974 Applied Superconductivity Conference, Oakbrook, Illinois, where I was a co-author of papers on the bronze-route material and solenoids already described. We still had a short period before we were due in New York to embark for home, so we toured through Canada visiting Niagara Falls, Ottawa and Quebec and then followed the fall colours down through New England.

Back at Harwell in late October, 1974, I became involved with Fraser Old in the study of the tensile properties of the $Nb_3Sn$ layers in the bronze-route material. We experimented on specially fabricated tensile specimens containing 343 filaments, heat treated to produce an $Nb_3Sn$ layer which in some cases occupied the whole filament. With all sample elastic behaviour up to about 0.15% strain was followed by plastic deformation. With a high volume fraction of filament (more than 16% by volume) the specimens broke at 0.5 - 0.8% strain but at lower volume fractions the plastic yielding continued to 0.9% and was followed by a region of approximately constant load. Metallographic examination showed cracks in the $Nb_3Sn$ layers only at strains beyond the start of the constant load region, the number of cracks increasing with the extent of the strain. Acoustic emission studies showed no emission until very shortly before the constant load region was reached, building up quickly to a fairly constant average level but with large fluctuations in intensity. The conclusion was that the $Nb_3Sn$ layers only start to fail at the surprisingly high strain of at least 0.7%, very high for a brittle intermetallic compound. We intended to do further work to confirm these conclusions but we both moved to other work before that was done.

I took up again the interest in ac losses stimulated by the work at ORNL and began to study the ac properties of our bronze-route composites at 4.2K. There were no firm proposals to employ these materials in ac conditions so I concentrated on trying to develop an understanding of their ac properties in terms of their dc properties and of other authors work on materials such as NbTi alloys. Paul Sikora worked with me during two successive summer visits and helped my understanding of theoretical aspects of the work.

Alternating current losses were measured on bifilar coils of twisted filament wire with or without an applied dc field, a lock-in amplifier being used to measure the lossy part of the voltage across the coil. In alternating field experiments, samples were either bundles of short lengths of wire (with untwisted filaments, for longitudinal field), or an open circuit coil of wire (with twisted filaments, for transverse field), and were inserted in a pickup coil located in an ac solenoid, again with an optional dc field. Once again a lock-in amplifier was used to measure the loss signal. Magnetisation loops could be measured on these samples by an electronic integration technique and the waveforms of the signals could be observed on an oscilloscope.

Reports of this work were presented at a number of conferences in the USA and in Europe. The ac behaviour of these materials is complex as indeed is the theory to which they should be compared, so no adequate summary can be given here. To be very brief, longitudinal field losses, with or without a dc bias field could be quite well correlated with existing theory if allowance was made for surface screening currents and surface roughness effects. Losses in transverse field did not fit any established theoretical models.

From the mid 70s the funding for the superconducting materials program at Harwell was gradually reduced and I began to work three of the five days each week on a program developing improved methods of ultrasonic inspection. My last Applied Superconductivity Conference was Santa Fe in 1980 and I transferred permanently to the ultrasonics project shortly after that.

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