The Manufacture of High Temperature Superconducting Tapes and Films

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<u>**ABSTRACT**</u>

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THE MANUFACTURE OF HIGH TEMPERATURE

SUPERCONDUCTING TAPES AND FILMS

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The potential benefits to society that might be gained if the promise of efficient energy technologies and ultra-fast computational technologies, through the development of superconductor technologies, can be realised are far reaching and exciting. However, if the opportunities arising from these exciting advances are to be grasped then difficulties in the large scale production of these brittle ceramic materials must be addressed. This thesis contributes to the body of knowledge that will enable a solution to this problem through consideration of two different manufacturing routes.

Firstly, an investigation was performed to examine the manufacture of high temperature superconducting tapes via a powder-in-tube technique. This initial study was concentrated on tapes manufactured from the recently discovered thallium-based superconducting material (Tl,Pb,Bi)-1223. Particular attention was paid to the microstructural evolution of the tapes' core with varying sinter temperature. It was found that the platelet-like as-prepared powder could be used to form superconducting tapes that displayed partial texturing - a feature not before observed in thallium-based tapes of this kind. The synthesised powder had an excellent intra-grain critical current density of 6.5×10^4 A cm^{-2} in an applied magnetic field of 1 T, at 77 K, with a superconducting transition temperature, T_C, of 110 K. Moreover, the powder was relatively simple to prepare – the achievement of reproducibility normally being a problem associated with the 'shake and bake' preparation of thallium materials. Transport critical current densities upto 5.6×10^3 A cm^{-2} in a magnetic field of 0 T, at 77 K, were measured in short lengths of tape. The problem of weak grain connectivity was observed.

The difficulties associated with the manufacture of long lengths of superconductor by the application of the powder-in-tube approach suggested that an alternative route might be more productive. A relatively new area of superconductor manufacture known as electrodeposition was therefore considered. A detailed study of the electrochemical fabrication of superconducting precursor films was performed. Fundamental measurements of the metals involved were carried out and then a range of precursor films synthesised and analysed in order to understand the electrodeposition process of multi-metal co-deposition. A range of major control parameters involved in the process where identified that affected both the intrinsic film characteristics and the process reproducibility. These parameters included ambient temperature, applied potential, deposition technique, and solution composition. A procedure was developed that yielded a highly reproducible process which allowed the production of quality films exhibiting void percentages from as low as 45 % and upto 90 %. Heat treatment of selected films resulted in high purity, highly aligned, Bi-2212 films with T_C's ~ 98 K, and multiphasic (Tl,Pb)-1223 films with T_C's ~ 115 K, and magnetic critical current densities of 4.99×10^5 A cm^{-2}, and 1.26×10^6 A cm^{-2} at 77 K, 1 T, respectively.

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Contents

Chapter 1:

Introduction

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1   Introduction

1.1   What is Superconductivity? - An Historical Overview

One of the most notable events in the physical sciences this century has been the discovery of high temperature superconductors by J. George Bednorz and K. Alex Müller in April 1986 whilst working at the IBM laboratories in Ruschlikon, Switzerland [1]. The discovery was the culmination of 75 years of intensive research performed by groups around the globe whose collective aim was to raise the temperature at which a superconductor becomes superconducting to greater and greater heights.   Before 1986 the highest transition temperature, T_C, achieved had been 23.2 K for Nb_3Ge in 1973 [2]. Bednorz and Müller's new compound, identified as a member of the La-Ba-Cu-O system, became superconducting at 30 K and this exciting find initiated the rush to discover further superconducting cuprate materials. This quest has yielded a variety of materials with T_C's as high as 133 K.

In 1908 a Dutch physicist named Heike Kamerlingh Onnes, of the University of Leiden, succeeded in liquefying helium for which he received the Nobel Prize for Physics in 1913. Three years later (1911) he found that, amazingly, the electrical resistance of Hg plummeted to zero at 4.2 K [3](Figure 1.1). He also noted that electric currents persisted in the Hg, in the absence of voltage, without causing the heating effects associated with resistance in conventional conductors.   The physics of superconductivity was born. Subsequent searches for superconductivity, triggered by his observations, began with studies of the elements which then extended to simple alloys and intermetallic compounds.

Of all the elements studied Nb has the highest T_C of 9.3 K, but higher values have been found in intermetallic compounds. For example, in 1941, a T_C of 16.0 K was found for NbN [4]. The transition temperature gradually rose to 23.2 K in 1973 for Nb_3Ge. A number of sulphur-containing phases were also found to exhibit superconductivity, such as the $Li_xTi_{1.1}S_2$ ($x = 0.1$ - 0.3; $T_C = 10$ - 15 K) [5] and $Mo_{6-x}A_xS_6$ ($A = $ Cu, Ag, Pb, Sn, Zn, Mg; $x = 0.9$ - 1.5; $T_C = 3$ - 13 K) [6] systems.   In 1975 the first

polymeric superconductor, (SN)$_x$, with T_C < 1 K was reported [7] and five years later, following a prediction by London forty years earlier [8], superconductivity in organic materials was discovered. Despite the prediction that a T_C of 100 K could be achieved in these materials [9] the current record stands at a lowly 8 K [10].
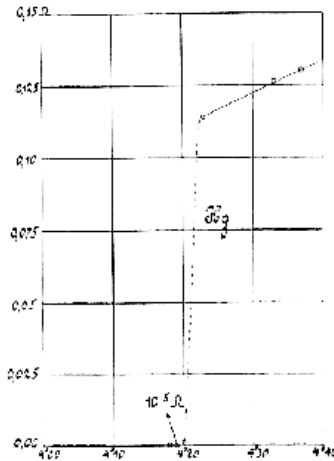
Figure 1.1   Resistance in ohms of a specimen of mercury versus absolute temperature. This plot by Kamerlingh Onnes marked the discovery of superconductivity (reference 3).

Investigations were also undertaken to observe super-conductivity in metal oxides. In 1964 the first superconducting oxides were reported with T_C's ≈ 1 K; these were TiO and NbO. SrTiO$_{3-x}$ with Nb doping was found to superconduct at 0.7 K [11]. The T_C was subsequently raised to 13 K with the discovery of the spinel LiTiO$_4$ [12], and the distorted perovskite Ba(Pb$_{1-x}$Bi$_x$)O$_3$ [13]. Undoubtedly, the most important result in the field of superconductivity was the discovery of superconductivity in a copper oxide based system, specifically La$_{2-x}$Ba$_x$CuO$_4$, as mentioned above (Figure 1.2). The importance of this discovery was immediately recognised by the scientific community by awarding Bednorz and Müller the Nobel Prize for Physics, less than one year after the publication of their findings. By the end of 1986 superconductivity research had achieved revolutionary advances with the effort of Paul C. W. Chu and colleagues at the University of Houston in America. Signs of superconductivity above 77 K were repeatedly observed in the poorly-

characterised samples during the period, strongly affirming the existence of superconductivity in the liquid-nitrogen temperature range. The scientific world knew that the textbooks had to be re-written after January 1987, when the Houston group, in collaboration with M. K. Wu, then at the University of Alabama at Huntsville, achieved stable and reproducible superconductivity in $YBa_2Cu_3O_{7-\delta}$ (Y123) (Figure 1.3), with a T_C close to 100 K [14]. Superconductivity at such high temperatures defied the common understanding of solids and as of 1996 the theory of high temperature superconductivity has yet to be formulated.
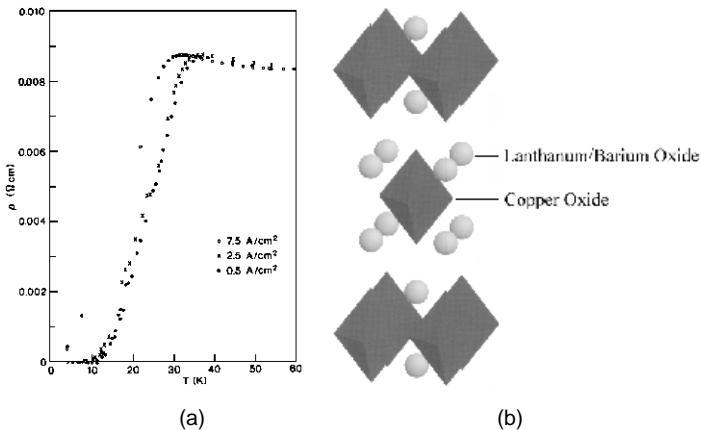
Figure 1.2 The first evidence of high temperature superconductivity. (a) The resistance versus temperature for $(Ln,Ba)_2CuO_4$, and (b) the crystal structure of $(Ln,Ba)_2CuO_4$.

Until 1987 the inconvenience, and expense, of liquid helium refrigeration meant that the widespread application of wires and tapes was considered economically unfeasible. However, with the advent of Y123 there were significant savings resulting from the displacement of liquid helium by liquid nitrogen for cooling. The race for new superconductors with higher T_C's continues. Bismuth- and thallium-based superconductors were discovered in 1988 [15,16] which become superconducting at 110 K and 125 K, respectively. The mercury-based compounds were discovered in 1993 [17], with transition temperatures upto 164 K under a pressure of 10^5 Pa. Many laboratories throughout the world have reported evidence for superconductivity at much higher temperatures, but these however, have yet to be confirmed conclusively.
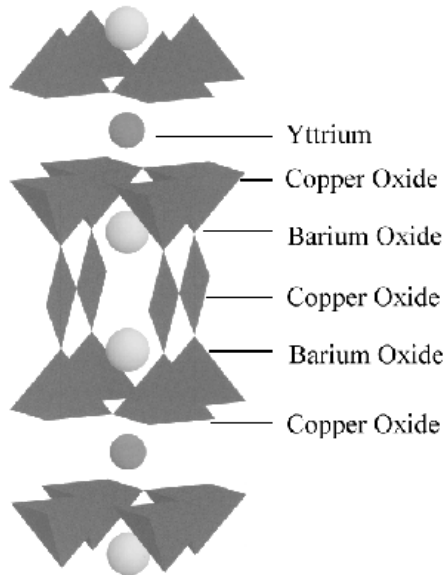
Figure 1.3 The crystal structure of Y123.

Very recently, three other classes of superconductor have been discovered, namely: fullerides, borate-/fluorine-containing compounds, and oxycarbonates. The fullerides, such as MC_{60}, are a totally unique family based on the curious carbon molecule Buckminster Fullerene, having T_C's of 18 K, 28 K, and 32.5 K for $M = K_3$, Rb_3, and Cs_2Rb, respectively [18]. Boron- and fluorine-containing compounds such as $LnSr_2Cu_{3-x}BO_7$ [19] and $Sr_{2-x}A_xCuO_2F_{2-\delta}$ (A = Ca or Ba) [20], members of the layered cuprate family, have T_C's of upto 64 K. Finally, the oxycarbonates, for example $(Y,Ca)_n(Ba,Sr)_{2n}Cu_{3n-1}O_{7n-3}CO_3$ (n = 2 - 4) [21], show yet another variation on the layered cuprate system.

Even though the liquid nitrogen barrier has been broken, many of the great promises of superconductivity technology have yet to be realised. The difficulties with the materials can be attributed to many of the material and engineering problems of high temperature superconductors (HTSC's), e.g. making long HTSC wire that can carry large currents without energy loss and can retain excellent properties over long periods of time without chemical and physical degradation. After the discovery of the transistor in 1947, it took almost 40 years to introduce the one

megabit memory chip which is vital to modern computers. Modern discoveries in superconductivity go far beyond piecemeal improvements in electric devices. Future applications that take advantage of the fascinating phenomena of superconductivity will cause significant changes in electricity generation, data transmission and storage; impacts in microelectronics, communication and computers; and advances in solid state science. This progress will only be achievable through determination and persistence, and this thesis is a contribution to that endeavour.

1.2 Superconducting Properties

We can usually associate the remarkable properties of superconductors with three words: zero, infinite and perfect. The most striking characteristic of a superconductor is the abrupt disappearance of electrical resistance below a critical temperature T_C - the state of infinite electrical conductance. Below T_C the material is said to be in its superconducting state and at a temperature above T_C the material is in its normal state. The absence of electrical resistance, however, does not completely define the superconducting state. In 1933 Walter Meissner and Reiden Ochsenfeld of the University of Leiden discovered that superconductors are perfectly diamagnetic as well as being perfect conductors [22]. This means that an applied field is completely excluded from the interior of a superconductor up to a critical field, H_C, whereupon the material resorts to its 'normal' metallic state. This differs from the description of a 'perfect' conductor. The behaviour of a perfect conductor (Figure 1.4), when subjected to a magnetic field at different temperatures, depends on the state of the conductor when the field is applied. If a perfect conductor, initially in zero magnetic field (a), is cooled below T_C (b) and moved into a magnetic field (c), then by Faraday's law of induction, eddy or surface currents are set up so as to repel the flux from the interior of the material. If however a magnetic field were applied before the temperature was reduced below T_C (e), the flux would still penetrate the whole of the conductor (f). After the applied field has been removed currents will flow in the surface of the conductor so that the magnetic flux through the sample will not change (g).

(a) $T > T_C$ (b) $T < T_0$ (c) $T < T_C$ $H_c > H > 0$ (d) $T < T_C$ $H = 0$

Resistive State   Resistanceless State   Magnetic Field Removed

Magnetic Field Applied

(e) $T > T_C$ $H > 0$ (f) $T < T_C$ $H_c > H > 0$ (g) $T < T_C$ $H = 0$

Resistive State Magnetic Field Applied   Resistanceless State   Magnetic Field Removed
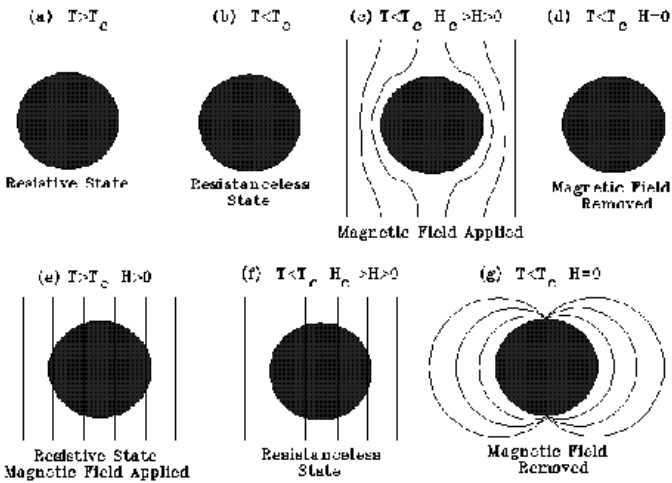
Figure 1.4 The magnetic behaviour of a 'perfect' conductor.

Meissner and Ochsenfeld found that when a superconductor is cooled below T_C in a magnetic field the flux is spontaneously expelled because surface currents flow that repel the field inside (Figure 1.5). The same effect is obtained if a magnetic field is applied to a superconductor below T_C. Removal of the applied field causes the persistent surface currents to disappear and hence the field associated with them (c) unlike the case for a perfect conductor. It follows from the Meissner effect that if the field inside the superconductor is zero the magnetic susceptibility, χ, of a superconductor (M/H) must be exactly -1. This is known as perfect diamagnetism.

(a) $T > T_C$ $H > 0$ (b) $T < T_C$ $H_c > H > 0$ (c) $T < T_C$ $H = 0$

Resistive State Magnetic Field Applied   Resistanceless State   Magnetic Field Removed
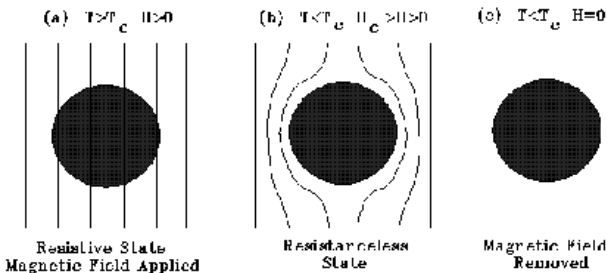
Figure 1.5 The magnetic behaviour of a superconductor.

The critical field, H_C, mentioned above, is observed to be related to the critical temperature T_C by the expression:

$$H_C = H_0\left[1-\left(\frac{T}{T_C}\right)^2\right]$$

{1.1}

where H_0 is the value of the critical field at 0 K (Figure 1.6). If the applied magnetic field is derived from an electrical current flowing in the superconductor, there is a corresponding critical current density, J_C, such that if $J > J_C$ then the material goes normal.

The abrupt change in resistivity at T_C in superconductors is only one of many abrupt changes that occur in the material. Figures 1.7a and b depict the temperature dependence of various selected properties of a superconducting material. Note that all the significant changes occur at T_C, and all highlight the striking changes that occur when a superconducting material passes from its normal state to its superconducting state.
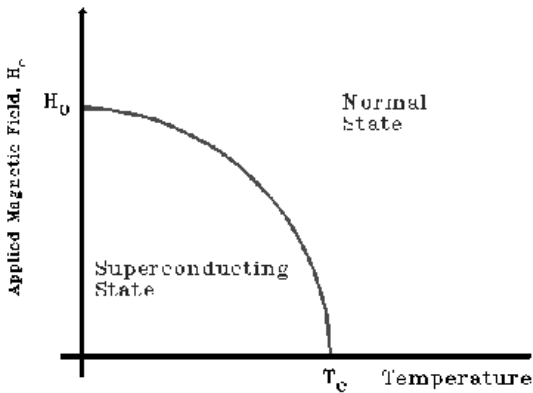
Figure 1.6 Typical relationship observed between the critical field and T_C for the elements.

Probably the most well-known superconducting property is the fact that the DC resistivity disappears at the critical temperature and remains zero below T_C. This is very different from conventional metals. In ordinary metals the resistivity, ρ, is proportional to T^5 at low temperatures. Also there is a remnant resistance as temperature approaches zero, i.e. the resistance never completely disappears.
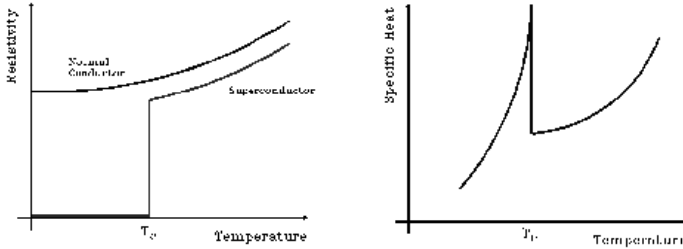
Figure 1.7a The temperature dependence of resistivity and specific heat in superconductors.
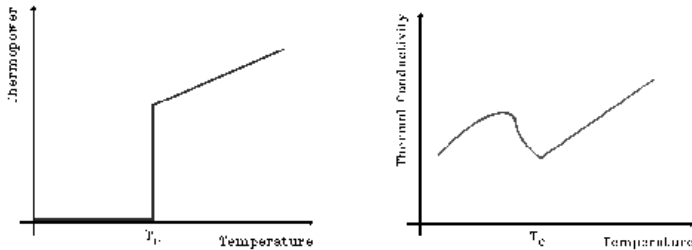
Figure 1.7b The temperature variation of thermopower and thermal conductivity in superconductors.

1.3   Type I and Type II superconductors

The magnetisation curve expected for a superconductor is shown in Figure 1.8. Pure specimens of many materials exhibit this behaviour; they are referred to as type I superconductors or, formerly, soft superconductors. The values of H_C are always too low for type I superconductors to have any useful technical application, in coils for superconducting magnets for example.

The second type of superconductors exhibit magnetisation curves of the type depicted in Figure 1.9. These are known as type II superconductors. Materials of this type tend to be alloys or transition metals with high values of electrical resistance in the normal state. Type II superconductors have superconducting electrical properties up to a field, H_{C2}[‡]. However, between the lower critical field, H_{C1}, and the upper critical field, H_{C2}, the Meissner effect is incomplete (i.e. $B_{internal} \neq 0$) and magnetic flux penetrates the superconductor.   In this region the

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[‡] H_{C2} may be 100 times higher than the value of the critical field, H_C, calculated from the thermodynamics of the transition.

superconductor is said to be in a vortex state, also known as the mixed state. An upper critical field of 41 T has been attained in an alloy of Nb, Al, and Ge at the boiling point of helium. It should be noted that in figure 1.9 a critical field H_C has been labelled. This critical field is the field as determined from thermodynamic considerations.
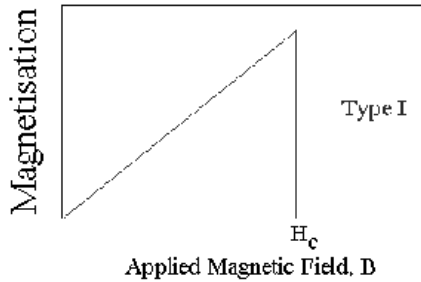
Figure 1.8 Magnetisation versus applied magnetic field for a bulk superconductor exhibiting a complete Meissner effect (perfect diamagnetism): a type I superconductor.
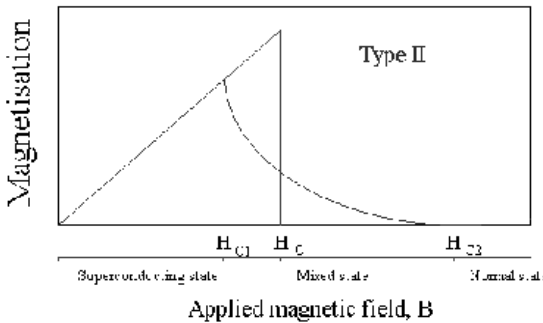
Figure 1.9 Magnetisation versus applied magnetic field for a bulk superconductor exhibiting an incomplete Meissner effect: a type II superconductor.

1.4   Theories of Superconductivity

A microscopic theory for conventional superconductivity was proposed in 1957 by Bardeen, Cooper, and Schrieffer [23,24] and is now known as BCS theory. The theory followed studies by Cooper of the "Cooper pair" where it was found that under certain conditions the ground state of energy of a pair of electrons is lower than that of the two free electrons. The central

result of the BCS theory is this energy gap of which the critical temperature, the thermal properties, and the magnetic properties are a consequence. The weak coupling of electrons is achieved by the mechanism of Frohlich interactions. Here thermal lattice vibrations (phonons) interact with the electrons causing a weak attractive force between a pair (the typical separation distance of a pair of electrons is of the order of 10^4 Å).

The theory accounts well for the equilibrium properties of conventional or low T_C superconductors and thus values for T_C, H_C, the specific heat, and the penetration depth can be accurately derived. Since the discovery of the new high-T_C superconducting oxides many new theories have been proposed to explain the high T_C's and observed physical properties. These include several theoretical non-phononic models, such as Anderson's resonating valence bond (RVB) model [25], the spin bag model by Schrieffer *et al.* [26], the charge excitation model (Varma *et al.* [27]), plasmon exchange models [28-30], and Wilson's direct on-site electron-pair coupling mechanism [31].

1.5   Manufacture of Superconducting Tapes and Films

One of the most important present aims in the field of superconductivity is the ability to produce continuous lengths of superconductor for applications ranging from current carriers, to superconducting high-field magnets. A variety of techniques have been employed in preparing superconducting tapes and films with varying degrees of success. These include molecular beam epitaxy [32], thermal deposition of metal carboxylates (dip coating) [33], spray-drying [34], ion beam sputtering [35], RF magnetron sputtering [36], sol-gel processing [37], laser ablation [38], and metalorganic deposition [39], powder-in-tube (PIT), and electrodeposition.

1.5.1   *Molecular Beam Epitaxy*

Electron beam evaporation was the first technique used in depositing HTSC films [40-43]. Separate sources for each of the metal components are required. Usually, e-beam guns with independent rate control and feedback of the sources are used. Technical difficulties arise, though, because of the need for high oxygen pressures which affects the functioning of the e-beam guns, and the mass spectrometers as well as the microbalances used for process control. Techniques designed to overcome

these difficulties introduce such levels of complexity that few cases are known to work successfully.

Molecular beam epitaxy (MBE) has so far proved to be one of the most complicated, expensive, and least successful techniques. The reason for pursuing MBE work on these complicated oxide systems is the possibility of acquiring greater understanding of the growth mechanism for the production of high quality crystals, but it is unlikely that this is a candidate for large scale fabrication of superconducting films.

1.5.2   Sputtering

Sputter deposition - either from diode sources, conventional magnetrons, ion-beam sources, and novel cathodes - has been widely used for making HTSC's [44-59]. Films can be sputtered either from multiple sources (elements, alloys, oxides) or from single sources. Sputter deposition offers an easy rate control. If non-reactive gases are used, the deposition rate of a sputter gun is almost proportional to the power of the electrical discharge and no feedback loop is needed to control the gun. However, the technique offers very low growth rates ~ 1.0 nm min^{-1}, and the extension to a continuous process is not clearly apparent.

1.5.3   Thermal Spraying/Deposition

This technique yields high deposition rates, ~ 1.0 μm min^{-1}, and has possible applications for a continuous deposition process, as well as for large areas. Deposited films are not epitaxial but can be highly textured achieving good critical current densities, e.g. 6×10^5 A cm^{-2} at 77 K for Y123 [33].

1.5.4   Laser Deposition

Pulsed laser deposition (PLD) is a relatively new technique [60-63]. As in the one-target sputtering process, a bulk sample forms the source. A ultra violet or visible high-energy laser pulse of 10^8 - 10^{10} W cm^{-2} and a duration of the order of 10 ns vaporises the material. A plume of constituents is ejected from the target and impinges on a substrate. The wavelength and the laser fluence have a decisive influence on the quality of the deposits. The highest quality Y123 epitaxial films have been grown to date using this technique. Problems do occur in depositing thallium-based films or lead-doped films because of their high volatility. The approach is, however, scalable.

1.5.5   Sol-Gel Techniques

Sol-gel techniques [64,65] and co-precipitation methods starting from solutions of the respective cations have been studied to avoid nitrate and carbonate contamination of grain boundaries, which is common in vapour deposition techniques using carbonate and nitrate targets. There is good control over the film content and cation distribution. High purity ceramics have been manufactured this way.

1.5.6   Powder-in-Tube (PIT) Method

PIT is a method whereby fully-reacted or partially-reacted powders of superconducting material are packed into Ag or Ag alloy tubes. The tubes are then drawn out to form wires, and then rolled to obtain tapes. After extensive research in short lengths of superconducting tape, tapes ~ 1 km in length and longer have been produced. The key problem with this approach is that homogeneity along the tape/wire is difficult to achieve. The root of this problem is the difficulty in preparing 100 % pure starting powders. If a normal state 'barrier' occurs along the tape then current carrying properties of the conductor are greatly affected. This has been overcome by producing multi-filamentary cores giving the super-current alternative routes. Texturing (grain alignment) is also hard to achieve, except in $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi-2223) based tapes due to the favourable morphology of this material. A great deal of work into this technique [66,83] has yielded promising results from mainly Y-123, Bi-2223, Bi-2212, and Tl-2223 based systems. Y-123 tape with a critical current density, J_C, of 3.33×10^3 A cm^{-2} at 77 K and in zero field has been fabricated [67]. The samples displayed very poor in-field behaviour though - the J_C fell to 1/100th of its zero field value with the application of only 20 mT. Bi-2212 wires have been prepared [68] with J_C's upto 1.2×10^3 A cm^{-2} in zero field at 77 K.

Wires prepared from the Bi-2223 material have yielded the most promising results thus far, with J_C's over 5.4×10^4 A cm^{-2} at 77 K in zero field with impressive J_C's of ~ 1.2×10^4 A cm^{-2} in an applied field of 1 T [77]. Despite the engineering problems with this method good results have been obtained and the area remains a very active research environment. A major application of Bi-2223 tapes is the manufacture of very high field superconducting magnets at 4.2 K.

1.5.7 Electrodeposition

Electrodeposition involves the deposition of relevant metallic cations, from a deposition solution, onto a conductive substrate by electrolysis [84]. The principle attraction of the technique is its already proven scalability. High quality, thick, films may also be obtained. This method is fully reviewed in Chapter 5.

One of the important properties of a superconducting film is it's transport critical current density. Films and tapes with extremely large critical current densities have already been prepared. However, these films are normally very thin ($< 1 \,\mu m$) and therefore the critical currents are small. If high critical current films are to be manufactured then methods that can synthesise much thicker films must be developed. The ability to form thick films must also be accompanied by the ability to fabricate continuous lengths of conductor.

1.6   The Scope of this Work

This thesis is concerned with the manufacture of HTSC films and tapes, in particular via the PIT and electrochemical approaches. Initially, the application of the PIT method to the fabrication of tapes from a new thallium-based superconductor, based on the Tl-1223 system, was explored. The single layer Tl-1223 system was selected because of it's low anisotropy and the low dependence of transport properties upon applied magnetic fields - both positive attributes when considering tape and film manufacture. Particular attention was paid to the morphological evolution of the tapes' cores. The problem of poor grain connectivity was identified and solutions proposed. The difficulties posed by this approach when considering a continuous process, such as tape homogeneity, steered the research toward a more versatile technique - electrodeposition.

The main subject in this work is the electrodeposition of superconducting films with particular emphasis on the optimisation of the deposition process, as opposed to the optimisation of the post-deposition heat treatment. This is not a well researched area (as can be seen by the review in Chapter 5), and hence the research herein deals with the mechanisms of the deposition process in order to achieve a high standard of reproducibility in producing a variety of superconductor precursor films. The heat-treatment of the as-deposited films has been

determined, and results are presented for the characteristics of the resulting superconducting films. Tl-1223 materials are difficult to make, when compared to many other systems, because of the volatility of thallium. For this reason, electrodeposited Bi-2212 samples were prepared initially in order to demonstrate the deposition process. Toward the conclusion of the research attempts were made to fabricate, for the first time via electrodeposition, (Tl,Pb)-1223 films. Superconductivity was successfully observed in both the above types of film, though no critical current densities were successfully determined.

1.7 Thesis Outline

The thesis proceeds with a description of the experimental equipment used to manufacture and characterise the samples fabricated. Chapter 3 reviews the literature for progress in PIT tape production and then describes the manufacture and characterisation of a new type of thallium-based tapes. The chapter closes with suggestions concerning future development.

Chapters 4, 5, and 6 all deal with the electrodeposition of superconductor precursor films. This starts with an investigation into the basic electrochemistry of the superconductor components, and then progresses onto the electrochemical synthesis of Bi-Sr-Ca-Cu, Tl-Ba-Ca-Cu, Ba-Ca-Cu, and Tl-Pb-Sr-Ca-Cu, and Hg-Ba-Ca-Cu superconductor precursor films. Experimental considerations were extensively researched with the implications for mass production kept in mind.

The penultimate chapter (7) deals with the superconducting properties of the heat treated films. Properties analysed were x-ray spectra (which also yielded data indicating the alignment and purity of the fabricated films), film morphology, superconducting transition temperature, and finally, the magnetic current carrying properties.

Finally, chapter 8 summarises the principal results obtained during the research, and an indication to the future of continuous superconductor production is presented.

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