High temperature superconducting tapes and current leads

Bernhard Zeimetz

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HIGH TEMPERATURE SUPERCONDUCTING

TAPES AND CURRENT LEADS

A thesis submitted in fulfilment of the requirements for the award of the degree

Doctor of Philosophy

from

UNIVERSITY OF WOLLONGONG

by

Bernhard Zeimetz, Diplom-Physiker

Institute for Superconducting and Electronic Materials

and

Department of Materials Engineering

March 1998
I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the award of any other degree or diploma of the university or other institute of higher learning, except where due acknowledgment is made in the text.

Bernhard Zeimetz

February 1998
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ABSTRACT

The scope of this thesis was (i) to contribute to the optimization of Bi2223 precursor powder and tape processing, and (ii) to design and test HTS current leads using Bi2223 tapes. Various steps of powder and tape processing, and their influence on final properties of tapes, were investigated, including powder stoichiometry, powder calcination and grinding, mechanical deformation and heat treatment of tapes. The Bi2223 grain size varied considerably between tapes made from different powders, and critical currents were found to increase with increasing grain size. An inverse relationship between the Bi2223 formation rate and the grain size was found. Silver, and especially silver addition to the core, were found to have a strong influence on Bi2223 texture and critical currents. Silver additions were also used as a ‘tracer’ to investigate powder flow during mechanical deformation. The formation of ‘sausaging’ during mechanical deformation was investigated in a parameter study, and found to be closely related to formation of shear bands and necking. It was demonstrated that Bi2201, forming at Bi2223 grain boundaries, caused depression of critical currents, but could be removed by appropriate processing. Various Bi2223 formation mechanisms were identified. Two sets of current leads were developed and tested, both allowing vapour cooling of the HTS tapes, tapering of the leads, and maximum flexibility of current capacity and heat leak by allowing exchange of individual tapes. The first pair of current leads was developed for a Superconducting Magnetic Energy Storage test facility at Monash University. The leads were successfully tested up to 200 A in a stray magnetic field of the SMES coil of 400 mT. In the second lead design, aimed at a current capacity of 2000 A, the HTS tapes were held by steel clamps in a circular arrangement. The leads were successfully tested using applied currents up to 900 A DC, but their current capacity was estimated to be several kA. An analytical formula for optimizing the length of HTS tapes in a tapered current lead was derived.
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Introduction

The work presented in this thesis was carried out at the Institute for Superconducting and Electronic Materials (I.S.E.M.) at the University of Wollongong, as part of the wider effort in the research in High Temperature Superconductors (HTS) and development of their applications. Since their discovery in 1986, HTS have found enormous interest in worldwide research and development, because of their fascinating physical properties, and their great potential for industrial applications. HTS are considered a key technology of the 21st century.

One of the most promising HTS applications is their use in wires and tapes, for loss-free transport of high electrical currents. In Australia, this technology is targeted by the consortium project "A Plan for Australian Technology in High Temperature Superconducting Wires", led by Metal Manufactures Ltd. in cooperation with the I.S.E.M. and the CSIRO. The work presented here is part of this consortium effort, aiming at optimization of the production of HTS tape conductors based on 'Bi2223'.

The second part of this thesis is concerned with the use of Bi2223 tapes in HTS current leads. A current lead is an electrical connection between a device kept at a cryogenic temperature and its current supply at room temperature. Current leads have become the first practical application of bulk HTS. Two different current lead designs, both based on HTS tapes, were developed and tested as part of this thesis.

The text is organised as follows: Chapter 1 gives a brief review of the properties and applications of HTS, and Chapter 2 a review of HTS current leads, consisting of a short theoretical overview and a comprehensive literature review of the HTS leads that have been built and tested to date. Chapter 3 introduces the experimental methods used for production and characterization of the HTS tapes, as well as for testing the current
leads. Chapter 4 presents results and their discussion of the efforts to optimize Bi2223 powder and tape processing. This includes powder stoichiometry (4.1), powder processing (4.2 and 4.3), testing of commercial powders (4.4), effects of the silver sheath and silver addition (4.5), mechanical deformation (4.6) and heat treatment of the tapes (4.7). Chapter 4.8 discusses, on a more fundamental level, the Bi2223 formation mechanism. Chapter 5 presents the two sets of current leads that were developed during this thesis, with their design and test results. The key results of this thesis are summarized in Chapter 6. References are tabled at the end of each chapter.

The results in Chapter 4 will show that powder and tape properties are closely related, and the process parameters are interdependent. Therefore, it was decided to present powder and tape processing not separately, but as one continuous process, always with the final tape properties in focus. The second strong correlation is that between the microstructural and superconducting properties, which are also presented without strict separation.
1. Properties and Applications of High Temperature Superconductors

The discovery of (La,Ba)$_2$CuO$_{4-x}$ as a superconducting compound with a critical temperature $T_c = 34$ K [1] in 1986 opened access to a new class of superconductors, which today are named (ceramic) high temperature superconductors (HTS). Shortly after this discovery, in early 1987, superconductivity was discovered in YBa$_2$Cu$_3$O$_7$ with $T_c = 90$ K, above the boiling point of nitrogen [2,3]. This meant an enormous progress for possible technical applications, as cooling with liquid nitrogen is drastically cheaper and technically easier compared to the use of liquid helium.

The potential application of HTS as a ‘perfect’ medium for transport and storage of electrical energy, and expectations to find room temperature superconductivity led to a major rush into a search for new HTS materials. Several research groups reported to have found compounds with $T_c$ close to room temperature (e.g. [4,5]), but such findings could not be confirmed, and the highest confirmed critical temperature to date (at ambient pressure) is $T_c = 134$ K of HgBa$_2$Ca$_2$Cu$_3$O$_x$ [6].

Furthermore, the high expectations regarding applications at 77 K were disappointed, after very low critical current densities ($J_c$) were found in preliminary measurements. The poor mechanical properties of HTS were identified as another major obstacle for almost all applications.

To date, more than 100 HTS compounds have been found, and the HTS family continues to grow [6]. Despite their large number, all HTS show strong similarities in their properties (see e.g. the reviews [6,7,8]):
• nearly all HTS are ceramics and copper oxide compounds

• their crystal structure is perovskite-like and based on copper oxide planes, as shown in Fig. 1.1.

• in their normal conducting state, HTS are metallic conductors with electron holes as charge carriers, based on hybride bands (Cu-3d and O-2p) in the copper oxide planes.

• due to the layered crystal and electronic structure, HTS show extreme anisotropy in their physical properties and material parameters; e.g. in the compound Bi$_2$Sr$_2$CaCu$_2$O$_8$ the electrical conductivity, $\sigma$, shows metallic behaviour along the copper oxide planes, but semiconducting characteristics in perpendicular direction, and the value of $\sigma$ is reduced by a factor $10^5$ [7].

• superconductivity is only found if the charge carrier (hole) density lies in a specific range around 0.1 - 0.2 holes per CuO unit; the hole density is adjusted by either doping of metals or adjustment of oxygen stoichiometry. With lower hole densities the materials become insulators and/or antiferromagnets; in the 'overdoped' case one finds 'ordinary' metals without superconductivity, as shown the schematic phase diagram in Fig. 1.2.

• all HTS are type-II superconductors, with very small coherence length $\xi \leq 10$ Å and large penetration depth $\lambda = 10^4$ - $10^5$ Å, and accordingly with very large upper critical field $B_{c2} > 100$ T and (thermodynamic) critical current density $J_c = 10^7$ - $10^8$ A/cm$^2$.

One can see from this short overview, that HTS have been extensively investigated. They have found great interest not only because of their commercial potential, but also their fascinating physical properties. In particular, large efforts have
been made to determine the microscopic origin of superconductivity in these compounds, and the validity of the classical BCS theory [9]. The list above could be further extended, with keywords such as d-wave pairing, antiferromagnetic ordering and two-dimensional superconductivity [7,9,10].

Fig. 1.1: Crystal Structure of the Bi-based HTS Bi$_2$Sr$_2$CuO$_5$, Bi$_2$Sr$_2$CaCu$_2$O$_8$ ("Bi2212") and Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ ("Bi2223") (from ref. [8])
Fig. 1.2: Generic phase diagram of HTS depending on oxygen stoichiometry (or charge carrier density) (from Ref. [7])
A feature of HTS that has drawn much attention is the behaviour of the flux line lattice (FLL) [11,12]. Due to the anisotropy, short coherence length and high 'operating' temperature, the FLL is very 'soft' in HTS compared to classical superconductors. This causes movement of flux lines caused by thermal activation or by a transport current. Numerous models exist to describe the dynamics of the FLL, such as flux creep, flux flow, vortex glass, and in particular there is controversy over the question whether the FLL undergoes a thermodynamical phase transition at a 'melting' or 'irreversibility' line \( B_{\text{m}}(T) \), which is much lower than the upper critical field \( B_{\text{c2}}(T) \) [12]. Regardless of the models, the movement of the FLL leads to energy dissipation, and is a major reason that the actual critical current in HTS is often found to be much lower than the thermodynamic \( J_c \).

The second major limit to critical current densities especially in bulk HTS are weak link grain boundaries. As a consequence of anisotropy and short coherence length, one finds that usually the critical current density \( J_c \) across a grain boundary is much lower compared to \( J_c \) within a single crystal. This \( J_c \) depression can be caused by a misalignment between adjacent grains, or by secondary phases or stoichiometric variations at the grain boundaries [13].

While thin films have been produced with \( J_c \) close to the thermodynamical limit, flux creep and weak links have been the main obstacles to producing 'bulk' HTS with high critical currents, which are required for many potential applications of HTS.

There is a large number of possible applications of HTS [14,15], which can be categorized into electrical power engineering [15,16,22] (high current/voltage cables [17], transformers, motors, current leads [18] and others), magnetic levitation devices, magnetic sensors (SQUIDS), electronics and computing[19,20], and microwave
transmission components [21]. The commercial market for HTS applications has been estimated to grow to 120 Billion $US per year in 2020 [22].

From a manufacturing point of view, these applications can be divided into ‘bulk materials’ (power engineering and levitators) and ‘thin film’ devices (sensors, electronics, computing, microwaves).

For each of these two groups, it was found that the manufacturing of useful material in a reproducible process is a demanding challenge, due to the complex material properties. This was particularly felt in efforts for production of long length conductors, i.e. wires and tapes, which are probably the application having attracted most attention and R&D effort, due to their potential use in many power applications.

It was found that the Bi - based HTS materials Bi$_2$Sr$_2$CaCu$_2$O$_8$ (“Bi2212”) and Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ (“Bi2223”) are most suitable for production of HTS conductors [23]. The “Powder In Tube” (PIT) process [24], where the HTS material is processed in a protective silver sheath, has so far been the most successful method to produce long length conductors.

Production of Bi2223 PIT tapes is one of the subjects of this work. The material properties are, compared to a “normal” metal, very complex, such is the production of the tapes. Table 1.1 lists those physical, chemical and mechanical properties which are the main obstacles for the production of long length conductors, and the solutions which have been developed as a part of the “powder in tube” process.

The issues touched in the table will be addressed more detailed in later chapters; here the emphasis lies on the fact that all the crucial properties listed in column 3 are closely related to the microstructure. Therefore, microstructural and chemical analysis play a central role in the efforts to optimize HTS tape properties.
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Table 1.1: Overview of main properties of HTS and their correlation with materials processing
References


2. Review of High Temperature Superconducting Current Leads

2.1 Introduction and Definition

A ‘current lead’ in our sense is an electrical connection between a superconducting device kept at a cryogenic temperature and its current supply at room temperature. In many cases the current has to be very high, up to several thousand Amperes. Thus a ‘classical’ current lead usually consists of thick copper wire or braid. As the superconducting device itself produces no heat, and the design of cryogenic dewars is very advanced, most of the heat loss, i.e. Helium consumption or refrigeration load, comes from the current lead. Thus current leads determine a great part of the running costs of a superconducting system, and therefore its theoretical analysis and optimization have found great interest in the literature.

The discovery of high temperature superconductors (HTS) makes it possible to replace a part of the copper with superconducting material. This drastically reduces the heat losses because a) the superconductor generates no resistive heat and b) all HTS are very poor thermal conductors compared to copper. The critical current densities required are not very high, and flexibility of the conductor not crucial either. Therefore current leads have become the first commercial application of HTS. Before reviewing the efforts to produce practical HTS current leads, however, a summary of their theoretical analysis will be given.

2.2 Review of Theoretical Analysis

As the optimization of a current lead is of great importance to minimize helium costs, current leads have been treated in great detail in the literature even in ‘pre-HTS’ times.
[1-5]. In most of these treatments, the superconducting case is ‘implicitly’ included as the zero-current case (zero ohmic losses) of a normal conducting lead.

Detailed treatments were given by McFee [1], Mercouroff [2] and especially comprehensive by Buyanov [3,4]. Wilson’s book on superconducting magnets [5] contains a chapter on current leads with a thorough review, and is considered today's standard reference.

After the discovery of HTS it was soon realized that they could partly substitute normal leads [6,7], and thus found new interest in theoretical analysis [6-21], now focusing on HTS/normal hybrid current leads. A particularly comprehensive review of different hybrid lead designs was compiled by Hull [10]. Numerical values for heat leaks in various designs were given by Albrecht et al. [14]. Dresner’s work [13] focused on cryostability (quench behaviour and burn-out protection), which, however, was addressed by most authors. AC losses were treated in a paper of Herrmann et al. [19], while Seol et al. [21] discussed the advantages of a tapered lead. Runde [16] discussed a particular case study, the use of HTS bus bars in an Aluminium plant. Uher [22,23] reviewed thermal properties of HTS, which are important for design considerations. Data for pure metals can be found in the comprehensive work of Ho et al. [73], while Fujishiro et al. [74] reported on the thermal conductivity of various silver-gold alloys.

The following short review is mainly based on Wilson’s and Hull’s works [5,9-11].

a) normal conductor

The heat flow in a ‘classical’, normal conducting current lead has two sources:

1. The ohmic loss

\[ Q_{\text{ohm}} = I \times V = I^2 \times R(T) \]  

(2.1)
CHAPTER 2: REVIEW OF HTS CURRENT LEADS

with current \( I \), voltage \( V \), electrical resistance \( R \) and Temperature \( T \);

2. The heat flow due to thermal gradient

\[
Q_{th} = A \kappa(T) \frac{dT}{dx},
\]

(2.2)

where \( A \) is the cross section, \( \kappa(T) \) the thermal conductivity, and \( \frac{dT}{dx} \) the temperature gradient. Note that the two equations are linked via the temperature dependance. The heat has to be removed by cooling the leads. In the following, only cooling by helium will be considered. In this case the cooling can be maintained in two different ways:

1. The current lead is only cooled at the lower end, where it is submersed into liquid helium, while the rest of the lead is thermally insulated. This design is called conduction cooled (CC) lead or self cooled lead.

2. The boiled helium gas flows along the lead and thus cools it over its entire length: vapour cooled (VC) lead.

The equilibrium condition leads to a differential equation:

\[
\frac{d}{dx} \left( A \kappa(T) \frac{dT}{dx} \right) + \frac{I^2 \rho(T)}{A} = M \frac{C_p(T)}{A} \frac{dT}{dx}
\]

(2.3)

with electric resistivity \( \rho(T) \), flow rate of He gas \( M \) and the specific heat of He \( C_p(T) \).

In the CC case the minimum heat leak is given by

\[
Q_{\text{min}} = I \sqrt{\frac{\int_{T_{\text{min}}}^{T_{\text{max}}} \kappa(T) \rho(T) dT}{2}}
\]

(2.4)

and the optimum ratio of length \( L \) and cross section \( A \)

\[
(L / A)_{\text{OPT}} = \frac{1}{I} \sqrt{\frac{\int_{T_{\text{min}}}^{T_{\text{max}}} \kappa(T) / \rho(T) dT}{2}}
\]

(2.5)

For copper and most other pure metals, the Wiedemann Franz law can be used:
\[ \kappa(T) \rho(T) = L_0 T, \]  

(2.6)

where the Lorenz number \( L_0 = 2.45 \times 10^{-8} \text{ W}\Omega/K^2 \).

Because \( L_0 \) is a universal, material-independent constant, it follows from equation (2.4) that the minimum heat leak per current \( Q/I \) is material-independent. It is also independent of the cross section, i.e. there is no advantage in leads with a variable cross section. However, the shape factor \( L/A \) strongly depends on the material.

For the VC case, the solution of (2.3) is more complex, but for a Wiedemann-Franz metal obeying equation (2.6) we arrive at the same conclusion: The minimum heat leak of a normal conducting current lead is independent of the material chosen, and there is no gain in using a variable cross section.

The choice of the material and the shape is therefore determined by another aspect, the cryogenic stability of the lead: It has to be ensured that after short term overcurrents the lead returns to a stable condition without burnout. An analysis of this problem [1] yields that

1. A conductor with a low conductivity is favorable to one with high conductivity.
2. The danger of cryogenic instability increases with the length of the lead.

Inserting the actual data shows that for the VC case the theoretical minimum \( Q_{\text{min}} \) for the heat leak is

\[ Q_{\text{min}}(\text{VC}) = 1.04 \text{ W/kA,} \]

and for a CC lead the minimum is

\[ Q_{\text{min}}(\text{CC}) = 47 \text{ W/kA.} \]

When comparing these values, however, one has to consider that for CC the He only has to be re-liquified at 4.2 K, while in the VC case it has to be recooled from room
temperature with a very low Carnot efficiency. However, it is always more economical to use VC leads [5].

Another important result following from the universality of the Wiedemann-Franz law (2.6) is that the voltage along an optimized metal lead at its optimum current is always 80 mV, regardless of the material. The voltage drop is a very good experimental criterion to test the optimization of a current lead.

b) superconductor

If the current lead is superconducting, the ohmic loss $Q_{\text{ohm}}$ is zero, and equation (2.2) can be integrated directly:

$$Q_{\text{s}} = A / L \int_{T_{\text{min}}}^{T_{\text{max}}} \kappa(T) dT$$  \hspace{1cm} (2.7)

Assume that the current lead operates at the critical current $I_c$ of the superconductor, and use $A = I_c / J_c$, one finds for the heat leak per current:

$$Q / I_c = 1 / (J_c L) \int_{T_{\text{min}}}^{T_{\text{max}}} \kappa(T) dT$$  \hspace{1cm} (2.8)

Table 2.1 gives some data for the integral

$$K(T_1, T_2) = \int_{T_1}^{T_2} \kappa(T) dT$$

between 4K and 77 K.

Table 2.1: Integral 4K -77K of thermal conductivity for some HTS and metals; the high purity data (*) are very sensitive to impurity concentration

<table>
<thead>
<tr>
<th>Material</th>
<th>Bi2212 melt cast</th>
<th>Bi2223 sintered</th>
<th>YBaCuO sintered</th>
<th>Copper high purity</th>
<th>Copper phos. deox.</th>
<th>Silver high purity</th>
<th>Silver-Gold alloy (At%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(4K,77K) [W/m]</td>
<td>65</td>
<td>80</td>
<td>230</td>
<td>70,000*</td>
<td>5000</td>
<td>200,000*</td>
<td>10,000 (1%) 1000 (10%)</td>
</tr>
<tr>
<td>Reference</td>
<td>[14]</td>
<td>[14]</td>
<td>[14]</td>
<td>[51]</td>
<td>[42], [73]</td>
<td>[73]</td>
<td>[74]</td>
</tr>
</tbody>
</table>
From Table 2.1 it can be seen that using HTS leads can drastically reduce the heat leak, and secondly, that in the case of silver-sheathed tapes, it is very advantageous to use an alloy sheath. It is also clear from Eq. (2.7) and (2.8), that in the superconducting case, tapering a current lead will reduce the heat leak.

2.3 Design and Properties of HTSC Current Leads: Literature Review

According to Eq. (2.8), in the superconducting case the heat leak depends on the length L, and on the superconducting \( J_c(T) \) and thermal properties \( \kappa(T) \) of the lead. These three parameters have to be considered for the design of the lead.

While the length L is usually determined by the size of the cryogenic system (and consideration of cryogenic stability [5], as discussed in the previous chapter), one has to maximize the Critical Current Density \( J_c \) and/or to minimize the thermal conductivity \( \kappa(T) \). Furthermore, due to the strong temperature dependance of \( J_c \) it is obvious that the heat leak can be reduced by choosing a variable cross section. Stability considerations are most important, as the superconductor can be quenched into the normal state and thus abruptly increasing its resistance, leading to a burn-out.

Numerous efforts to produce efficient HTS current leads have basically diverged into two directions: One can either produce bulk rods or tubes of HTS such as YBaCuO(123), Bi2212 or Bi2223, with a rather low \( J_c \), but very low \( \kappa(T) \). Another possibility is to utilize silver sheathed HTS tapes, with high \( J_c \) and high \( \kappa(T) \) (of the silver sheath). In the latter case the thermal conductivity can be drastically reduced by using alloyed silver, as shown in table 2.1.

However, the comparison must not be limited to physical properties \( J_c \) vs. \( \kappa \), but include some engineering considerations [77]. Important advantages of tapes are:
• low resistance contacting (joining) is achieved by conventional soldering (while it is a major problem for 'bulk' HTS)

• tapes can be aligned such that the influence of an external magnetic field on $J_c$ is minimized

• silver works as mechanical and chemical protection

• danger of quenching is strongly reduced due to high thermal/electrical conductivity of silver

• variable cross section is simply achieved by stacking tapes with different lengths

The major advantage of bulk materials is an economic one, as they are much cheaper and easier to produce. Costs of tape production are further driven upwards, when alloyed sheath material is used. The second important choice is that between vapour cooling and conduction cooling. Furthermore, one can consider to cool the non-superconducting part, usually copper, with liquid nitrogen, which further decreases He consumption. On the other hand, vapour cooling and additional nitrogen cooling make the design and engineering of a cryogenic system more complex.

Table 2.2 summarizes the available literature on HTS current leads, sorted by research groups. Included, if available, are current capacities, HTS current densities, heat leaks and cooling design. In some cases, the HTS leads were successfully implemented into cryogenic applications, such as SMES, magnets, current limiters etc.
<table>
<thead>
<tr>
<th>Research Groups (Europe)</th>
<th>Material(s)</th>
<th>length [cm]</th>
<th>$I_c$ [A]</th>
<th>$J_c$ [A/cm$^2$]</th>
<th>heat leak Q/I [mW/kA]</th>
<th>cooling mode / application(s)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uni Cambridge (UK)</td>
<td>2212 bulk on substrates</td>
<td>10 - 20</td>
<td>200 - 1000</td>
<td>1000 (77 K)</td>
<td>50 mW / 200 A</td>
<td>CC Cryocooler Nb$_3$Sn magnet</td>
<td>[24]</td>
</tr>
<tr>
<td>Oxford Instruments (UK)</td>
<td>2212 bulk (Hoechst)</td>
<td>12</td>
<td>1000 (60 K)</td>
<td></td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>Alcatel Alsthom (FR) + Rhone Poulenc (FR) + Siemens (GER) + Hoechst (GER)</td>
<td>(a) 2212 bulk (b) 2223 bulk (c) 123 (sintered) (d) 123 MTG</td>
<td>(a) 50 (b) 40 (c) 20 (d) 5</td>
<td>(a) 2000 (b) 1000 (c) 600 (d) 550</td>
<td>(a) 20 (b) 90 (c) 430 (d) 800</td>
<td>VC</td>
<td>[14],[26-28]</td>
<td></td>
</tr>
<tr>
<td>GEC Alsthom (FR)</td>
<td>(a) 123 sintered (b) 123 MTG</td>
<td>(a) 12 (b) 5</td>
<td>(a) 300 (b) 550</td>
<td>(a) 250 (b) $10^4$</td>
<td></td>
<td></td>
<td>[29]</td>
</tr>
<tr>
<td>Hoechst AG (GER)</td>
<td>2212 bulk (melt cast)</td>
<td>20 - 80</td>
<td>2000</td>
<td>2000</td>
<td></td>
<td>VC / LHC orbit magnets (800 !)</td>
<td>[30-32]</td>
</tr>
<tr>
<td>CERN Geneva (CH)</td>
<td>2212 bulk (Hoechst)</td>
<td>10</td>
<td>&gt; 25</td>
<td></td>
<td></td>
<td>CC LHC CERN</td>
<td>[33]</td>
</tr>
<tr>
<td>CERN Geneva (CH)</td>
<td>(a) 2223 tape (ASC) (b) 123 fibres (EURUS) (c) 123 bulk bar (Haldor) (d) 2212 bulk (Hoechst)</td>
<td>(a) 50 (b) 20 (c) 30 (d) 20</td>
<td>12500 (required)</td>
<td>(a) 140 (b) 600 (c) 530 (d) 470</td>
<td></td>
<td>CC LHC CERN</td>
<td>[34]</td>
</tr>
<tr>
<td>Uni Birmingham (UK)</td>
<td>123 sintered</td>
<td>15</td>
<td>&gt; 100</td>
<td>500 - 1000</td>
<td></td>
<td></td>
<td>[35]</td>
</tr>
<tr>
<td>Uni Goettingen (GER) + Siemens (GER)</td>
<td>123 thick films (IBAD)</td>
<td>10 - 20</td>
<td>$\simeq$ 5000</td>
<td>$10^5$</td>
<td></td>
<td>Current limiter</td>
<td>[72],[76]</td>
</tr>
<tr>
<td>Research Groups (USA + Japan)</td>
<td>Material(s)</td>
<td>length [cm]</td>
<td>( I_\text{c} ) [A]</td>
<td>( J_\text{c} ) [A/cm²]</td>
<td>heal leak Q/I [mW/kA]</td>
<td>cooling mode / application(s)</td>
<td>References</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-------------</td>
<td>-------------</td>
<td>----------------</td>
<td>----------------</td>
<td>-----------------</td>
<td>-----------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>TCSUH</td>
<td>(a) 2223 bulk</td>
<td>(a) 15</td>
<td>(a) 800</td>
<td>(a) 530</td>
<td>(a) 900</td>
<td>VC / SMES</td>
<td>[52][53] [67]</td>
</tr>
<tr>
<td></td>
<td>(b) 123 bulk (sintered)</td>
<td>(b) 15</td>
<td>(b) 300</td>
<td>(b) 240</td>
<td>(b) 300</td>
<td></td>
<td>(a) [54-56]</td>
</tr>
<tr>
<td></td>
<td>(c) 55 (HTS)</td>
<td>(c) 55</td>
<td>(c) 1500</td>
<td>(c) 1000</td>
<td>(c) 100W/16kA</td>
<td></td>
<td>(b) [57-60]</td>
</tr>
<tr>
<td>Argonne National Lab [[(c) with Babcock &amp; Wilcox Co.]]</td>
<td>(a) 123 bulk</td>
<td>(a) 20</td>
<td>1000</td>
<td>(a) 250</td>
<td>600</td>
<td>VC</td>
<td>(c) [61,62]</td>
</tr>
<tr>
<td></td>
<td>(b) 2223 bulk</td>
<td>(b) 15-25</td>
<td>1500</td>
<td>(b) 1000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(c) 2223 tape (Ag-Au)</td>
<td>(c) 55</td>
<td>16000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Westinghouse Co.</td>
<td>(a) 123 bulk</td>
<td>(a) 15 (HTS)</td>
<td>(a) 500-1800</td>
<td>(a) 250</td>
<td>( \equiv 600 )</td>
<td>VC</td>
<td>(a) [63-64]</td>
</tr>
<tr>
<td></td>
<td>(b) 2212 bulk</td>
<td>(b) 60</td>
<td>(b) 1500</td>
<td>(b) 1000</td>
<td></td>
<td></td>
<td>(b) [64-66]</td>
</tr>
<tr>
<td>Naval Research Lab Washington</td>
<td>(a) 123 bulk</td>
<td>20</td>
<td>(a) 170</td>
<td>( \equiv 250 )</td>
<td></td>
<td>VC</td>
<td>[68]</td>
</tr>
<tr>
<td></td>
<td>(b) 2223 bulk</td>
<td>(b) 250</td>
<td>(b) 1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>General Electric Co.</td>
<td>123 MTG</td>
<td>( \equiv 6 )</td>
<td>150</td>
<td>300</td>
<td>660</td>
<td>CC Cryocooler</td>
<td>[69]</td>
</tr>
<tr>
<td>Los Alamos National Lab</td>
<td>123 thick film (on YSZ)</td>
<td>100 - 400</td>
<td>420</td>
<td></td>
<td></td>
<td>CC Cryocooler Magnet</td>
<td>[70,71]</td>
</tr>
<tr>
<td>Fuji Electric</td>
<td>2223 bulk</td>
<td>15</td>
<td>1000</td>
<td>250</td>
<td></td>
<td>VC</td>
<td>[36][37]</td>
</tr>
<tr>
<td>Railway Technical Research Institute</td>
<td>2223 tape (Ag-Au)</td>
<td>43</td>
<td>600</td>
<td>550</td>
<td></td>
<td>CC / Maglev train magnets</td>
<td>[38]</td>
</tr>
<tr>
<td>Toshiba</td>
<td>123 MTG</td>
<td>10</td>
<td>3100</td>
<td>( \times 10^4 )</td>
<td>3W/5500 A</td>
<td>VC</td>
<td>[39]</td>
</tr>
<tr>
<td>Sumitomo Heavy Industr. + Tohokuni Sendai</td>
<td>2223 bulk</td>
<td>10</td>
<td>1000</td>
<td>&gt;1000</td>
<td>150</td>
<td>CC Cryocooler</td>
<td>(a) [40][41]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(a) I_c test unit</td>
<td>(b) [42-44]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(b) 11T magnet</td>
<td></td>
</tr>
<tr>
<td>Sumitomo Electric Ind.</td>
<td>(a) 2223 tape</td>
<td>(a) 55</td>
<td>(a) 500-2000</td>
<td>( \equiv 10^4 )</td>
<td>(a) 300</td>
<td>CC / SMES, synchrotron</td>
<td>(a) [45-48]</td>
</tr>
<tr>
<td></td>
<td>(b) 2212 MTG</td>
<td>(b) 20</td>
<td>(b) 4000</td>
<td>( \equiv 10^3 )</td>
<td>(b) 160</td>
<td></td>
<td>(b) [49][50]</td>
</tr>
<tr>
<td>Showa Electric Wire Co.</td>
<td>2223 bulk (Ag addition)</td>
<td>10</td>
<td>1130</td>
<td>2500</td>
<td>( \equiv 100 )</td>
<td></td>
<td>[51]</td>
</tr>
</tbody>
</table>
The list of research groups in Table 2.2 is dominated by company names, showing that a high commercial potential is attributed to HTS current leads (commercially available leads are listed further below). It is also remarkable that many groups consider two or more possible materials in their research. Clearly, a single favourite material has not (yet) emerged.

Of particular interest to this question are investigations of various materials from a 'neutral' point of view, such as that of CERN [34]. CERN wants to utilize HTS leads for its Large Hadron Collider (LHC), and invited commercial suppliers to enter their 'products' into a comparative test (required capacity 12.5 kA). Preliminary results [34] showed surprisingly that the ASC design based on Bi2223 PIT tapes has the lowest heat leak, compared to the 'metal-free' bulk designs. Another, very comprehensive comparison of different materials and designs was carried out by the European collaboration of Alcatel, Rhone-Poulenc, Hoechst and Siemens [14,26-28].

A new, third material group besides 'bulk' and tape-based HTS current leads has emerged recently: YBCO thin films on Ni substrates show very high current densities ($10^6$ A/cm²) and current capacities up to 5000 A [72,76]. These are very attractive superconducting properties; however, heat leak data are not yet available. Table 2.2 also shows a wide range of current capacities. They reach from 25 A for LHC orbit magnets (800 pairs of leads required!) [33] to 16000 A for an electric utility SMES [61,62].

It must be emphasised that the quality criterion for a current lead is not simply the current capacity or critical current density, but the heat leak per current, as discussed in the previous chapter. The listed data clearly show the economic benefit of HTS leads, as in most cases the heat leak per current was 50-90 % below the theoretical optimum of copper leads (1.04 W/kA).
All the leads in the list based on HTS tapes were made with alloyed sheath, and in all cases a silver-gold alloy was used. This demonstrates that finding a suitable, cheap alloy material, which is also important for other reasons, proved to be a difficult task. Using gold is, of course, making the tape and thus the current lead considerably more expensive.

The highest heat leaks were generally found in YBCO leads (as expected from thermal data, cf. Table 2.1), and particularly in melt textured YBCO leads, which also are always very short, due to the production process. Longer leads can only be obtained by sintering. Tapered leads were produced from Bi2223 tapes [45-48], but apparently not (yet) with bulk material.

Demonstration of HTS leads in practical applications, as shown by some of the groups, is most important to move HTS from cryogenic laboratories into industrial use. In particular, HTS current leads have a 'strategic' significance for applications of both HTS and low-T_c superconductors, in helium-free cryocoolers [77]. These rely on relatively small refrigeration losses, and therefore in many cases they can only be used in combination with HTS leads. Therefore, HTS current leads greatly increase the potential use of superconductors in cryocooler applications.

Meanwhile, HTS leads are not only a research object, but are available as a commercial product, based on melt-cast Bi2212 (Hoechst AG, Germany and Westinghouse, US), sintered Bi2223 (CAN Superconductors, Czech Republic), Bi2223 tapes (American Superconductors Corp.), or Y123 multifilament fibres (EURUS Technologies, US).
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(Proc. of ASC Boston Oct 16-20, 1994)


3. Experimental Methods

3.1 Production of Bi2223 Precursor Powders

The first, and perhaps most crucial step in the production of high quality Bi2223 conductors is the preparation of precursor powders with sufficient purity and homogeneity, and the desired phase composition and particle size distribution. This is a considerable challenge, and in fact most groups working on Bi2223 tapes confine themselves to using commercially available powders.

The straightforward production method for ceramic powders is the 'solid state route', where oxides or carbonates of single metals (in our case Bi\textsubscript{2}O\textsubscript{3}, PbO, SrCO\textsubscript{3}, CaCO\textsubscript{3} and CuO) are mixed and reacted by repeated grinding and sintering [1][2]. In the case of Bi2223, however, one relies on extreme homogeneity of the mixture, as will be seen in later chapters. Therefore, wet-chemical methods are preferably used. Here the starting materials are dissolved in an acidic solution, and then the solution is solidified in various ways, depending on the specific process. The methods include co-decomposition [3], co-precipitation [4], spray-drying [5], spray-pyrolysis [6] and freeze drying [7]. This ensures, in theory, atomic level mixing of the components.

In the course of this work, two methods were used: co-decomposition and spray-drying of solutions in nitric acid. In both cases, nitrates (or oxides and carbonates) of the five metals were weighed carefully according to the desired stoichiometry, and dissolved in nitric acid. In the case of co-decomposition, the amount of liquid used (HNO\textsubscript{3} and deionized water) was kept at a minimum, to minimize the processing time. The solution was solidified by boiling at circa 100 °C. During the solidification, the liquid, which
became a slurry, was mixed with a magnetic stirrer. In the final stage, when the slurry became almost solid, the stirrer had to be removed.

Spray-drying is a method of rapid solidification, by spraying the liquid into a heated chamber, together with nitrogen gas. An aspirator pump creates a high speed gas flow, pumping the resultant powder into a second chamber, where it is collected. For the experiments in this thesis, a YAMATO PULVIS GB22 spray dryer was used. It allows control of liquid spray rate, gas flow speed, and inlet (spray) temperature. All these parameters strongly influenced the quality of the powder, as well as the nitrates' concentration in the solution. For the latter, it was found that a lower concentration resulted in improved quality of the powders, so that here the concentration was chosen well below the solubility limit. This was also found to prevent blocking of the spray nozzle, and reduced corrosion of the aspirator pump.

In both cases, co-decomposition and spray-drying, the resultant powder was a mixture of nitrates, which, when exposed to air, absorbed moisture very fast and became liquid again. It was therefore essential to move the powder as quickly as possible into a preheated furnace. The first powder calcination (770 - 800 °C) had to be carried out in a fume hood, because the nitrates decomposed into oxides, releasing nitric acid fumes.

The calcination/sintering was followed by grinding, carried out either by hand in an agate mortar, or in a planetary ball mill, with agate or zirconia jars and balls. During grinding, absorption of moisture was again a major problem, as well as particle agglomeration, as will be discussed in Chapter 4.

The sequence of sintering (in an alumina jar with a lid) and grinding was repeated 2 - 4 times, until the desired phase composition and homogeneity were reached. It was essential to minimize contamination with e. g. iron, silicon, moisture, or CO₂. All these have a strongly detrimental effect on the final properties of the Bi2223 tapes [8].
3.2 Production and Processing of Bi2223 Tapes

The production of Bi2223 ‘Powder-In-Tube’ tapes broadly consisted of three steps: (i) filling of powders into silver tubes, (ii) mechanical deformation (with intermediate annealing), and (iii) sintering (with intermediate deformation). In the first step, the powder was filled into a pre-cleaned silver tube. Tubes used in this work had an outer diameter of 6.5 mm and a wall thickness of either 0.5 mm or 1 mm. Before filling, they were cleaned with alcohol in an ultrasonic bath, and dried and deoxidized with a short annealing. To densify the powder in the tube, the tubes were tapped on a steel plate, or in some cases, a steel rod was used to ram the powder, which of course leads to a higher initial powder density. The other main parameter determining the filling density is the powder particle size distribution. Depending on powder and filling technique, filling densities varied between 20 and 40 percent of the theoretical density.

After filling, the tube was annealed at 400 - 600 °C, to remove moisture and /or CO\textsubscript{2} from the powder. The open end was then closed with a lid. The deformation procedure involved two stages. The first step was to reduce the tube diameter, by either drawing or groove rolling (‘square rolling’). Drawing was carried out with round dies, a speed of 7.5 cm/sec and reduction rates around 15 percent per pass. During groove rolling, the wire was rolled through a hexagonal or square shaped groove (ca. 5 - 8 cm diameter, linear speed 5 cm/sec), with reduction rates of 15 -20 % per pass. After drawing or groove rolling, the wire had a diameter of 1 - 2 mm.

The second part of the deformation was flat rolling, resulting in a tape with 100 - 300 μm thickness and 2 - 4 mm width. For flat rolling, three rolling machines were available, with roller diameters 25 mm, 55 mm and 230 mm. For the latter, the rolling speed could be varied, while the two other machines had fixed speeds of 5.0 cm/sec. The deformation rate was varied between 5 and 30 percent, to investigate its influence on
tapes. During the deformation process, the wires/tapes were annealed at 400 - 500 °C, to prevent cracking of the silver sheath (which is much softer than the oxide core). Despite annealing, cracks were observed in some tapes, depending on filling density and deformation route.

Sintering of tapes was carried out in tube furnaces, which were carefully calibrated in terms of absolute temperature and temperature profile. To achieve reproducible superconducting properties, the temperature has to be kept in a narrow range of 1-2 °C. The calibration was repeated regularly. The standard heat treatment consisted of 2 sintering stages (around 840 °C for 30 - 60 h), with an intermediate deformation. The deformation was either performed by rolling, as described above, by uniaxial pressing with 1 - 2 GPa, or by ‘sandwich rolling’, where the tape is rolled between two steel plates [9]. For longer tapes, the two latter methods were not used. The thickness reduction of intermediate deformation was 15 - 20 %, which in the case of rolling or sandwich rolling was accomplished in two rolling passes.

To investigate the Bi22223 formation, some tapes were heat treated only for short periods, and then fast cooled. For these heat treatments, a gold-coated quartz tube furnace was used, which has a much lower thermal mass and therefore a much higher self cooling rate of 50 °C/min, compared to 2 - 4 °C/min for ‘ordinary’ furnaces with alumina tube and ‘Kaowool’ insulation.

3.3 Characterization of Bi2223 Powders and Tapes

3.3.1 Microstructural and Chemical Analysis

It was pointed out in chapter 1 (Table 1.1, page 9) that microstructural and superconducting properties of Bi2223 tapes are closely linked, and therefore microstructural analysis plays a central role in efforts to optimize tape processing.
When working on the improvement of the tapes, it is therefore insufficient to measure the "critical current" or other electromagnetic properties alone; because these are determined by the microstructure. Only microstructural investigation allows one to determine which factor e.g. limits the critical current, and which part of the processing has to be improved. This relationship is again depicted in table 3.1.

Table 3.1: Correlation between processing, microstructure and superconducting properties in 2223 tapes

<table>
<thead>
<tr>
<th>Production</th>
<th>Microstructure</th>
<th>Electrical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder processing +</td>
<td>phase purity</td>
<td>critical current</td>
</tr>
<tr>
<td>Powder-In-(Ag)Tube</td>
<td>grain alignment</td>
<td>$I_c(T,B,\omega,...)$</td>
</tr>
<tr>
<td>Deformation</td>
<td>density</td>
<td></td>
</tr>
<tr>
<td>+</td>
<td>microcracks</td>
<td></td>
</tr>
<tr>
<td>+</td>
<td>oxygen vacancies</td>
<td></td>
</tr>
<tr>
<td>+</td>
<td>core-silver interface</td>
<td></td>
</tr>
<tr>
<td>Heat treatment</td>
<td>...</td>
<td></td>
</tr>
</tbody>
</table>

X-Ray Diffraction (XRD) is by far the fastest and most convenient way for microstructural characterization of Bi2223 tapes. Samples are easily prepared by peeling of one side of the silver sheath, and a typical measurement takes 30 - 60 minutes. The diffraction pattern allows the determination of the chemical phase composition, and a semi-quantitative estimate of the grain alignment.

The relatively high background 'noise', however, limits the accuracy. A chemical phase can only be detected if its volume ratio exceeds a few percent, and if the grain size is at least around 1 \( \mu \text{m} \). Therefore very small amounts of secondary phases can not be
detected. Another disadvantage of XRD, as of all the methods discussed here, is the irreversible ‘damage’ of the tape sample (This problem can be overcome with the use of a tunable synchrotron X ray beam [10]). It also has to be kept in mind that, due to the sample preparation, the measurement is taken in a region of the core which is close to the interface to the silver. As the silver plays an important role in the Bi2223 formation, this region along the interface may not be representative for the bulk of the core [11].

Closely related to XRD is the X Ray Texture Analysis technique which allows a more accurate determination of the grain alignment by measurement of pole figures.

Optical Microscopy and Scanning Electron Microscopy (SEM) allow direct observation of the microstructure. While the resolution of the optical microscope is limited to circa 1 µm, the SEM can provide information of the structure in the sub-micron range. An important tool in electron microscopy is Energy Dispersive (X Ray) Spectroscopy (EDS) which allows identification of chemical phases and their stoichiometry.

The main difficulty of microscopy is in the sample preparation, i.e. to provide a cross section through a tape which reveals its ‘true’ structure. The brittle, polycrystalline oxide ceramic (with density less than 100 %), and the very ductile silver sheath are a very challenging combination for metallographic work. Sample preparation includes mounting, grinding, polishing, etching and coating (for SEM) of the samples. Each of these steps bears the possibility of changing the true structure. For example, shrinkage of the mounting resin or grinding can ‘simulate’ cracks in the core; smearing of the silver by improper polishing can alter the apparent core-sheath interface, or over-etching can produce ‘artificial’ secondary phases. Even very diligent preparation cannot fully exclude the possibility of these and other effects, and they always have to be kept in mind when assessing a sample.
For measurements of cross section areas, and in particular superconductor-silver ratio of the tape cross section, an image analysis system was used in conjunction with an optical microscope. These measurements, however, proved to be rather inaccurate, as the obtained value depends strongly on the polishing/etching of the sample, and on the brightness of the microscope's light bulb. The error is estimated to be 20%, and this means that also critical current density data contain a similarly large error.

Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM) are new techniques which have been developed in the last decade. They can provide structural information ranging from micrometer scale to imaging of single atoms. Like electron microscopy, they require careful sample preparation, with the same qualifications as discussed above.

Differential Thermal Analysis (DTA) and Thermogravimetry (TG) are mainly used for characterization of precursor powders. They provide a very reliable and direct assessment of the quality of a precursor, which cannot be obtained by any of the other methods discussed. This is due to two facts: DTA is a (very rough) simulation of the 'real' (isothermal) sintering process, which can be influenced by very small amounts of secondary phases or impurities. Secondly, DTA tests the bulk of a sample, rather than a chosen surface.

Particle Size Analysis (PSA) allows measurements of particle size distribution of precursor powders. For a measurement, the powder is poured into a liquid solution (most commonly water) and the distribution determined with the aid of a laser beam. Particle size is a crucial property influencing the reactivity of the precursor, and thus the 'optimum' heat treatment. However, the PSA measurements were sometimes impeded by agglomeration of the powders, which even with the built-in ultrasonic stirrer could not be dissolved.
Appendix: Equipment used for microstructural and chemical analysis

**X Ray Diffractometer (XRD)**

Philips PW1730 generator, Philips PW 1050 Goniometer (Θ - 2Θ) with graphite monochromator

Radiation: Cu K (others possible), Filter: Ni

**XRD Texture Analysis**

Philips PW1729 generator, PW 1087 Goniometer (ϕ - χ)

Radiation: Co

**Scanning Electron Microscope (SEM)**

Leica Stereoscan S440

LINK Oxford EDS Detector

**Atomic Force Microscope / Scanning Tunneling Microscope (AFM/STM)**

Digital Nanoscope IIIa

**Differential Thermal Analysis / Thermogravimetry (DTA/TG)**

Setaram TGA 92-16.18

scan rate typical 10 C/min; TG resolution 1μg

**Particle Size Analysis (PSA)**

Malvern Mastersizer

Range: 50 nm - 800 μm
3.3.2 Electromagnetic Characterization of Bi2223 Tapes

The single most important property of a HTS tape for any application is its critical current density \( J_c = \frac{I_c}{A} \). \( J_c \) is a function of temperature \( T \), magnetic field \( H \), AC frequency \( \omega \) and other parameters. It can also depend on the history of the tape, for example whether it was zero-field cooled or field cooled in a magnetic field.

While for fundamental investigations, one considers only the current density per superconducting cross section \( (A = A_{SC}) \), for applications the total cross section of the tape \( A_{TOT} = A_{SC} + A_{silver} \) is more relevant. In the latter case, one speaks of the engineering current density \( J_e = \frac{I_c}{A_{TOT}} \). As was mentioned in the previous chapter, the superconducting cross section could only be determined with a high error of ca. 20%, and therefore \( J_e \) data contain the same error. Therefore, in the course of this thesis, \( I_c \) values will be given in most cases.

The standard critical current measurement was carried out at 77 K in liquid nitrogen (LN\(_2\)) with 1\( \mu \)V/cm criterion. Current sources with current limits of 10 A (Keithley 228A) and 100 A (Hewlett Packard 6672A) were available. The standard resolution of the voltmeters (Keithley DMM 196 and Keithley 2000/2001) was 0.1 \( \mu \)V. For \( I_c \) measurements in magnetic fields, 2 magnets were available, with capacities of 40 mT and 1 T, respectively. A four-probe technique was used, to exclude contact voltages. In most cases, the tape was contacted by clamping with office clamps. Sometimes clamping caused problems, (i) if the critical current was high, causing contact heating which was accompanied by a thermal voltage, (ii) if the clamp was magnetized, being the source of an external magnetic field. For more accurate measurements, the tapes had to be soldered onto the sample holder.
A computer program in C++ was written to perform computer-controlled $U(I,B)$, $I_c(B)$ and other measurements, avoiding long and repetitive manual measurements. Furthermore, the computer measurements were saved in files which could be directly read by standard graphics software.

Some tapes were sent to I. Kusevic and E. Babic, at the University of Zagreb in Croatia, for $I_c(B,T)$ measurements at other temperatures than 77 K, and resistivity measurements $R(T)$.

Critical temperatures were also determined by AC susceptibility measurements in a Quantum Design Physical Properties Measurement System (PPMS). The PPMS was also used to measure magnetization loops of tapes. From these, $J_c$ can be calculated with the Bean model, and compared with transport $J_c$ measurements.

### 3.4 Testing of HTS Current Leads

Two types of current leads were designed with HTS tapes: The first pair was built for a Superconducting Magnetic Energy Storage (SMES) system at Monash University, Melbourne. The current capacity targeted was 100 Amperes. The second type was a prototype current lead designed for currents up to 2000 Amperes.

In both cases, the tests consisted of two main parts: Preliminary tests in liquid nitrogen, and then the actual performance test in a helium dewar. Voltage taps were attached at several points along each of the leads, so that current-voltage characteristics of all components and connections between them could be measured separately.

For the 200 A leads, the design and first tests in liquid nitrogen were performed at the University of Wollongong. They were then taken to Monash University, and tested in the SMES dewar. The test was first carried out in zero field, and then with the SMES coil connected. The current source for these tests had a capacity of 200 A, and the
voltmeter resolution was limited to 1 mV. These limits were found to be significant restrictions of the tests. However, it should be considered that successful tests and application in the 'real world' of the SMES environment have a significance of their own, in helping to bring HTS devices from the lab into commercial use.

The 2 kA lead was tested in Wollongong, where a HP Current source with 875 A current limit was available. A Voltmeter Keithley 2000 with a 10 channel Multiplexer was used. Utilizing computer controlled measurements (with a C++ program) was found to be particularly useful in conjunction with the multiplexer, due to the large amount of collected data. For the test in helium, an existing He dewar was re-designed. A detailed description will be given in Chapter 5.

References


4: Bi2223 Powder and Tape Processing

4.1 Powder Stoichiometry

4.1.1 Introduction: Phase Relations and Phase Diagrams

The production of Bi2223 Powder-In-Tube (PIT) tapes involves a large number of processing steps, and almost all of them have a strong influence on the final superconducting properties. Naturally, the powder stoichiometry is the first set of parameters to choose, and is among the most important ones.

The final microstructure, and in particular the phase purity of the Bi2223 phase, depend on the initial stoichiometry. Different Secondary Phases have very different influence on superconducting properties. Obtaining phase diagrams of the 6-component system Bi-Pb-Sr-Ca-Cu-O is a huge experimental task. Nevertheless, several research groups have worked on partial phase diagrams [1-6, 14, 18, 19], usually by considering metal oxides as components, as in Fig. 4.1.1, and by investigating bulk samples in air. Hence, the oxidation state and oxygen partial pressure are not treated as variables in these investigations. This is an important simplification, because they have a strong influence on phase relations (Chapter 4.3) and especially on the stability region of the Bi2223 phase [7]. It was also found that silver has a strong influence on Bi2223 formation (Chapter 4.5). Consequently, the material behaves quite differently in silver-sheathed tapes compared to air. Phase diagrams obtained from bulk samples in air cannot be applied directly to PIT processing. They can be used as a qualitative guide to find the 'optimum' stoichiometry. Recently, Majewski et al. attempted to consider the influence of oxygen and silver on the Bi2223 homogeneity region [18].
Phase relations are made even more complicated by the instability of the Bi2223 phase. It has been observed that Bi2223 decomposes when slow-cooled from its sintering temperature [15]. The Bi2223 phase, like most other oxide HTS, is thermodynamically unstable. It belongs to the group of 'entropy-stabilized' compounds [8]. The necessary entropy is 'supplied' by crystal defects. Conforming with this, it has been found that all Bi-based HTS compounds do not form with their ideal stoichiometry [6,8], as shown in fig. 4.1.1.

Comparative surveys of Bi2223 powder stoichiometrics used by various groups in PIT tapes [4][9] show some variation between the compositions, but generally all choose a shift from the 'ideal' composition Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ along the same lines:

- Pb replaces Bi in the ratio $\equiv 0.4 / 1.8$
- 'surplus' of Bi+Pb $\equiv 2.2$
- deficiency in Sr $\equiv 1.9$; and/or unequal ratio Ca / Sr $\equiv 2.2 / 2.0$

Lead is used as dopant because it has been found to stabilize the Bi2223 phase by changing the atomic distance in the BiO layers [16]. Recent work by Majewski et al. [2,18] clarified that a Strontium deficiency and excess Bismuth (and Copper) stabilize the Bi2223 phase. However, most compositions chosen by tape producers lie outside the homogeneity regions proposed by Majewski et al. [2], indicating that besides phase purity, other factors too have an important influence on the superconducting properties of the tapes. This was also confirmed in the investigations presented in the next chapter.
Fig. 4.1.1: Stoichiometric points, denoted as full circles, and homogeneity regions of the phases Bi2223 (+), Bi2212 (□) and Bi2201 (O) in a section (CuO = 25 mol%) through the quaternary phase diagram SrO - CaO - Bi2O3 - CuO in air. 'Intergrowth' regions are denoted as (*). (adapted from Ref. [6])
4.1.2 Variation of Copper Content and Bismuth-Lead Ratio

As a part of this thesis, two lines of stoichiometric variation were investigated:

1) The Copper content was varied from 3.05 to 3.16
2) The Bismuth / Lead ratio was changed from 1.85 / 0.35 to 1.9 / 0.32

The content of Strontium and Calcium was kept constant at 1.9 and 2.03, respectively.

The stoichiometries are summarized in Table 4.1.1. Powder P1 can be considered the ‘standard’ stoichiometry used at the ISEM in Wollongong.

The powders were produced by spray drying of nitrate solutions, and calcinated four times at 800 - 820 °C with intermediate grindings by hand in an agate mortar. (Powder processing will be discussed in Chapters 4.2 and 4.3). The influence of the two variables ‘Copper content’ and ‘Bismuth/Lead ratio’ was analyzed by DTA and XRD, and by producing and investigating PIT tapes from the powders.

Table 4.1.1: nominal stoichiometry of 4 powders investigated; L = “Low”, H = “High”
* The absolute copper content is uncertain, as explained in the text

<table>
<thead>
<tr>
<th>Powder # (+ internal #)</th>
<th>Bi/Pb ratio</th>
<th>Copper content</th>
<th>Bi</th>
<th>Pb</th>
<th>Sr</th>
<th>Ca</th>
<th>Cu* [3/(2.5) H2O]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1 (P6B1C4)</td>
<td>L</td>
<td>H</td>
<td>1.85</td>
<td>0.35</td>
<td>1.9</td>
<td>2.03</td>
<td>3.05 (3.16)</td>
</tr>
<tr>
<td>P2 (P7B7C4)</td>
<td>L</td>
<td>L</td>
<td>1.85</td>
<td>0.35</td>
<td>1.9</td>
<td>2.03</td>
<td>2.94 (3.05)</td>
</tr>
<tr>
<td>P3 (P8B1C3)</td>
<td>H</td>
<td>H</td>
<td>1.9</td>
<td>0.32</td>
<td>1.9</td>
<td>2.03</td>
<td>3.05 (3.16)</td>
</tr>
<tr>
<td>P4 (P9C4)</td>
<td>H</td>
<td>L</td>
<td>1.9</td>
<td>0.32</td>
<td>1.9</td>
<td>2.03</td>
<td>2.94 (3.05)</td>
</tr>
</tbody>
</table>

The last column of table 4.1.1 with Cu content contains two numbers, reflecting the uncertainty regarding the Cu content. The copper nitrate hydrate which was used as raw material, is labelled by some suppliers as

\[
\text{Cu (NO}_3\text{)}_2 \cdot 3 \text{ H}_2\text{O},
\]
but by others as

\[ \text{Cu (NO}_3\text{)}_2 \cdot 2.5 \text{H}_2\text{O} \, . \]

It can be assumed, however, that the real composition was the same in chemicals from all suppliers. In the literature, one also finds both formulas, depending on the source [10,11]. When calculating the amount of copper nitrate needed, one arrives at two different results, depending on the formula used. Table 4.1.1 gives both results. Copper nitrate was found to absorb water very readily when exposed to air, adding to the uncertainty of the true composition.

Fig. 4.1.2 shows XRD spectra, and fig. 4.1.3 DTA scan of the four powders after the final heat treatment. The effect of increasing the Bi/Pb ratio was visible as a reduction of \( \text{Ca}_2\text{PbO}_4 \) peaks in XRD patterns of powders P3 and P4 compared to P1 and P2. The DTA measurement suggested a decrease in the onset temperature for (partial) melting for powders with higher Bi/Pb ratio. This observation was somewhat contradicting the decrease in \( \text{Ca}_2\text{PbO}_4 \), as usually \( \text{Ca}_2\text{PbO}_4 \) is considered to 'supply' liquid phase during the heat treatment and \( \text{Bi}_{2223} \) formation [12,13]. Removal of \( \text{Ca}_2\text{PbO}_4 \) should rather increase the onset of melting. However, in the literature there is no direct evidence given of the composition of liquid phase, and the melting may well have been generated by other phases. This point is further discussed in Chapter 4.3, where two powders with varying \( \text{Ca}_2\text{PbO}_4 \) content are investigated.

It also appears from the XRD measurements that the increase in Bi/Pb caused a slightly increased formation of CuO. In contrast, the direct reduction of Cu content (P2 vs P1 and P4 vs P3) had no apparent effect on the CuO content in the final powder. The DTA scans showed no significant difference between powders P1 and P2, but an additional peak shoulder appeared in the scan of P4 compared to P3. The results regarding the Cu variation were inconsistent with each other.
Fig. 4.1.2: XRD measurements (Cu K radiation) of the four powders after the final heat treatment
Fig. 4.1.3: DTA measurement of four powders after the final heat treatment; scan rate was 10 °C / min
The 4 powders were used to produce PIT tapes. The effect of the two stoichiometric variables on the final critical current (I_c) of the tapes, which is shown in Fig. 4.1.4, was rather small. All I_c differences were within 10%. The current density (J_c) all tapes was around 12 kA/cm². It can be seen from Fig. 4.1.4a that the increase of Bi/Pb ratio led to an increase in critical current, while the effect of changing the copper stoichiometry was ambiguous.

Fig. 4.1.5 shows XRD scans, and Fig. 4.1.6 SEM micrographs of tapes after the first sintering stage (50 h at 840 °C). The XRD scans of a tape with high Cu stoichiometry (P1) showed a higher CuO and (Sr,Ca)₂Cu₂O₅ content compared to (P2). This difference was seen much clearer in the SEM pictures. The tape with P2 had much fewer large cuprate particles (black). In the case of low Bi/Pb ratio (P1 vs. P2), lower Cu content led to smaller amount of cuprate phases. In the tapes with high Bi/Pb ratio, this difference was much reduced. The SEM micrograph of the tape from P4 had somewhat reduced cuprate particles compared to P3, but they were still present. The XRD measurements confirmed this, as CuO peaks were still visible in the scan of (P4) in Fig. 4.1.5. This means that there is a correlation between the formation of cuprate phases and Bi- or Pb-containing phases. As mentioned above, it was also found in the green powders that the Bi/Pb ratio influenced the appearance of CuO. The comparison of two other powders in Chapter 4.3 shows a similar result: reduced amount of Ca₂PbO₄ was accompanied by an increase in CuO (Fig. 4.3.1). Clearly, there is a (complex) interdependence between the two stoichiometric variables.

The SEM figures showed that large secondary phase particles had a strongly detrimental effect, as they reduced the superconducting cross section, and disturbed the alignment of Bi2223 particles. In Chapter 4.2 it is shown that these large (Sr,Ca)₂Cu₂O₅ particles formed from agglomerated CuO during the tape sintering.
Both XRD measurements and SEM micrographs showed that in the tapes with a high Bi/Pb ratio (P3 and P4), there was more Bi2201, but less Ca2PbO4 present. Bi2201 could be seen as white phase in the SEM micrographs, and had a strongly detrimental effect on superconducting properties, as will be discussed in Chapter 4.7.

The most important microstructural feature was the difference in Bi2223 grain size. The tapes with high Bi/Pb ratio (P3 and P4) clearly had much larger Bi2223 grains. This should have had an influence on the superconducting properties, as larger grain size means reduced number of grain boundaries, which are one of the limiting factors of the critical current (see Chapter 1). It is possible that this was offset by a larger amount of secondary phases (Bi2201 and cuprates) in these tapes.

The increased grain size must have resulted from a decrease in Bi2223 nucleation rate, which in turn is closely related to the question of Bi2223 formation mechanism (see Chapter 4.8). A correlation to the reduction of Ca2PbO4 phase in the powders and tapes with high Bi/Pb ratio seems possible. This would conform with the ‘standard model’ of Bi2223 formation which assumes that Ca2PbO4 decomposes into a liquid phase, which then reacts with Bi2212 into Bi2223 [13,15]. Reduction of Ca2PbO4 would result in reduction of liquid phase, and this would cause reduced nucleation of Bi2223. However, in chapter 4.3 a comparison between two powders with different Ca2PbO4 shows the opposite result, i.e. smaller grains in a powder with lower Ca2PbO4 content. Grivel et al. [17] compared Pb-doped and Pb-free Bi2223 samples (in air), and found that crystal size is significantly larger in Pb-doped Bi2223. Hence, the influence of lead and Ca2PbO4 on Bi2223 grain size is not clear at this stage. The influence of the tape sintering temperature on grain size will be discussed in the next chapter.
Fig. 4.1.4: Final critical currents of monofilament tapes made from powders P1 - P4 as function of Bi/Pb ratio (A) and Cu content (B); only data points which are connected can be compared to each other, as various fill factors and deformation routes were used. The critical current density of all tapes was around 12 kA/cm² (total tape cross section ≈ 0.2 x 3.5 mm²).
Fig. 4.1.5: XRD scans after first tape sinter (50 h at 840 °C), of monofilament tapes made from powders P1 - P4
Fig. 4.1.6 a,b: SEM (backscattering) micrographs of PIT tapes made from Powder P1 (high Cu content; low Bi/Pb ratio)
Fig. 4.1.6 c,d: SEM (backscattering) micrographs of PIT tapes made from Powder P2 (low Cu content; low Bi/Pb ratio)
Fig. 4.1.6 e,f: SEM (backscattering) micrographs of PIT tapes made from Powder P3 (high Cu content; high Bi/Pb ratio)
Fig. 4.1.6 g,h: SEM (backscattering) micrographs of PIT tapes made from Powder P4 (low Cu content; high Bi/Pb ratio)
4.1.3 Correlation with Tape Sintering Temperature

For each of the four stoichiometries, the influence of the tape sintering temperature was tested, by subjecting short samples to different temperatures and examining the microstructure and superconducting properties. Critical current as a function of tape sintering temperature is shown in Fig. 4.1.7, for tapes made from powders P1, P2 and P4. The results for tapes from powder P3 are not shown, because problems with the temperature calibration of the furnaces impeded the experiments. Fig. 4.1.7 shows that for powder P1 the highest critical current was found at a sintering temperature of 837 °C, while in tapes made from P2 and P4, 840 °C was the optimum tape sintering temperature. (The absolute critical current values of the tapes can not be compared, due to different fill factors. The critical current density in all tapes sintered at optimum temperature was around 12 kA/cm²).

Although the difference in optimum tape sintering temperature between the stoichiometries was small, it appeared that reduction of the copper content (from P1 to P2) allowed a higher sintering temperature, while increase in Bi/Pb ratio (from P2 to P4) had practically no effect. From the phase diagram proposed by Majewski et al. [2], which is shown in Fig. 4.1.8, one would expect that the optimum temperature for Bi2223 formation would decrease with increasing Bi/Pb ratio, as the Bi2223 homogeneity region (as function of Pb content) is ‘tilted’ for temperatures below 850 °C. The stoichiometries used in this thesis, however, are not represented in the section shown in Fig. 4.1.8.

Fig. 4.1.9 shows SEM micrographs of tapes made from powder P2, sintered at 835 and 844 °C, respectively. The difference in the microstructure, particularly in Bi2223 grain size, is very small. It appears that the sintering temperature, in contrast to the stoichiometry, has very little, if any, influence on Bi2223 grain size.
Fig. 4.1.7: Critical current against tape sintering temperature for tapes from powder P1, P2 and P4; The absolute values of the critical currents are not comparable, all optimum current densities were about equal (12 kA/cm²)
Fig. 4.1.8: Partial Phase diagram of the BiSCCO system, with Bi/Pb content and Temperature as variables; from Ref. [2]
Fig. 4.1.9: SEM micrographs of tapes made from powder P2, sintered for 40 hours at 835 °C and 844 °C, respectively.
4.1.4 Summary

Two variations of Bi2223 powder stoichiometry were investigated: copper content and Bi/Pb ratio. The stoichiometric changes are interdependent and lead to quite dramatic changes in the tape microstructure, but only small variation of critical currents. It is reasonable to suppose that the critical current in these tapes was limited by other factors. The potential benefits especially of increasing the Bi2223 grain size by varying the Bi/Pb stoichiometry could be much larger, and have to be further investigated. The variation of stoichiometry had very little influence on the optimum tape sintering temperature, and the tape sintering temperature was found to have little influence on the Bi2223 grain size. Other aspects of Bi2223 grain size are discussed in Chapters 4.3. and 4.4.

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IoP Publishing Conference Series No 158 (1997) 941


4.2 Powder Processing

4.2.1 Co-Decomposition and Spray-drying of Powders

In order to obtain powders with a high degree of homogeneity, wet-chemical methods are preferably used to mix the starting powders. The starting components are dissolved in diluted acid, and then re-solidified. As part of this thesis, two methods were tested: co-decomposition and spray drying.

For comparison of the two methods, two powders were solidified by co-decomposition and spray drying, respectively. The two powders were then heat treated three times, with intermediate grindings. The heat treatment sequence was 10 h at 770 °C + 10 h at 770 °C + 10 h at 820 °C. Fig. 4.2.1 shows SEM micrographs of powders made by co-decomposition and spray drying, taken after the third calcination. Both powders consisted mainly of small, platelike Bi2212 crystals, but the co-decomposition powder contained some large (>10 μm) particles consisting of Ca2PbO4 and (Sr,Ca)xCu1Oz. Such large particles were not found in the spray-dried powder. The SEM observations were further confirmed by a particle size measurement using laser diffraction, which is shown in Fig. 4.2.2. Both powders had a bi-modal particle size distribution, but the spray-dried powder had a slightly smaller particle size. However, these measurements were taken after two sintering stages and grinding, so that the effect of the initial solidification was partly disguised by the subsequent powder processing. The effects of grinding, and the problems of particle size analysis will be further discussed in chapter 4.2.3. The SEM allows a more direct observation, and here the spray-dried powder appeared to be more homogeneous.
Fig. 4.2.1: SEM micrographs of powders made by co-decomposition (A) and spray-drying (B)
During the solidification of the co-decomposition powder, some phase segregation could also be observed directly. Towards the end of the solidification process, the magnetic stirrer, which was used to mix the liquid, stopped moving because of the increasing viscosity of the slurry, and had to be removed. In the final stage of the solidification a green-blue layer was observed on the surface of the slurry, in contrast to the dark blue colour in the bulk. Such a segregation could be somewhat expected, as the different metal nitrates have different solubilities.

Segregation was not found in the spray-dried powders themselves, but agglomeration of CuO particles was observed in the green tapes made from some of these powders (depending on the Cu stoichiometry, see Ch.4.1). Fig. 4.2.3 shows some examples of such CuO agglomerates.
Fig. 4.2.3: Green tapes made from spray-dried powders, showing agglomeration of CuO particles (dark grey)
It is unlikely that the agglomeration of CuO occurred during powder grinding or the mechanical deformation of the tapes, and the only explanation left is a phase segregation during spray-drying. A phase segregation could have been the result of an 'instability' of the spray drying machine during operation, such as a pressure drop or a temperature change in the chamber. The stable operation of the spray drier was found to be very sensitive to its various operation parameters, which had to be carefully adjusted and monitored.

During the tape sintering at 840 °C, the CuO was transformed into $\text{Sr}_{x}\text{Ca}_{y}\text{Cu}_{z}\text{O}_w$. This is demonstrated in Fig. 4.2.4a, which shows a tape sintered for only 1 hour. The dark grey agglomerate in the center of the photograph consisted of two phases, CuO in the centre and $\text{Sr}_{x}\text{Ca}_{y}\text{Cu}_{z}\text{O}_w$ near the edge. The transformation was obviously incomplete after 1 h. At the end of the first sintering stage, shown in Fig. 4.2.4b, $\text{Sr}_{x}\text{Ca}_{y}\text{Cu}_{z}\text{O}_w$ could be seen as large, dark particles in a matrix of Bi2223 (grey needles). Bi2223 grains were partly grown through the cuprate particles. It was shown in chapter 4.1 that these cuprate agglomerates can be reduced by adjusting the Cu stoichiometry.
Fig. 4.2.4: Cuprate agglomerations in tapes after 1h (A) and 35 h (B) of sintering; in A the cuprates appear grey and Bi2212 light grey, while in B cuprates are black; grey needles = Bi2223, white = Bi2201
4.2.2 Powder Calcination

After the re-solidification of the nitrates, the powders were heat treated to form the desired phase composition. The heat treatment was carried out in 2 - 4 stages with intermediate grinding, in order to maintain and/or increase the powder homogeneity. All powders discussed in this chapter were heat treated in air. The influence of the sintering atmosphere is investigated in Chapter 4.3.

Starting from nitrates, the Bi2223 phase formed in a sequence of reactions which can be shortly described as [1]

\[
\text{Nitrates} \rightarrow \text{Oxides} \rightarrow \text{Bi2201 + SP} \rightarrow \text{Bi2212 + SP} \rightarrow \text{Bi2223}.
\]

(SP = secondary phases)

The final step of this sequence, the formation and growth of Bi2223 had to be withheld until the tape sintering. This was necessary to avoid and heal the defects introduced by the deformation process. The desired final phase composition of the precursor powder was a mixture of mainly Bi2212 with secondary phases. As the Bi2223 formation in air is known to occur in the temperature range 830 - 870 °C [2], the powder heat treatment must be carried out below 830 °C.

Some secondary phases were undesirable, as they were found to be very stable, requiring long tape sintering periods in order to be transformed into Bi2223. One of these phases is (Bi,Pb)3Sr2Ca2CuOy, shortly referred to as 3221 phase. Fig. 4.2.5 shows XRD patterns of two powders after the first and second calcination. The first powder was heat treated for 13 h at 770 °C and then for 8 h at 820 °C. The heat treatments of the second powder were carried out at higher temperatures: 24 hours at 800 °C and then 12 h at 810 °C. The main difference in the resultant phase composition was the occurrence of 3221 in the first powder after the first heat treatment at 770 °C. Moreover, the 3221
phase was still present after the second sintering stage at 820 °C. In the second powder no 3221 was detected. It follows that 3221 forms only at temperatures below 800 °C, but once it has formed, it is also stable at temperatures above 800 °C. W. G. Wang et al. [3] have shown that 3221 has strongly detrimental effects on the properties of the final tapes. Therefore, the powder sintering should be carried out at temperatures at or above 800 °C. To avoid the formation of both Bi2223 and 3221, a temperature window between 800 and 830 °C was found to be desirable for the powder calcination.

In both powders shown in Fig. 4.2.5, Bi2201 had formed during the first sintering stage, but was removed in both cases during the second sintering, probably through transformation into Bi2212. Similar to 3221, Bi2201 has a strongly detrimental effect on final tape properties ([4,5,6] and Chapter 4.7), but in contrast to 3221 it can be removed by sintering at 810 - 820 °C.
Fig. 4.2.5: XRD patterns of two powders after the first and second calcination
In order to minimize the process time, it is desirable to keep the number and times of the heat treatments at a minimum. A powder with stoichiometry Bi$_{1.85}$Pb$_{0.35}$Sr$_{1.5}$Ca$_{2.03}$Cu$_{3.05}$O$_{10+x}$ was produced by spray drying and subsequent calcination at 800 °C for 24 h, at 810 °C for 12 h and 820 °C for 24 h, with intermediate grinding. The powder properties after each heat treatment were investigated by XRD, DTA, and the powder performance assessed in the form of PIT tapes. XRD investigations on a powder after two and three heat treatments, shown in Fig. 4.2.6, suggested that apparently the phase composition did not change significantly during the third heat treatment. Both XRD patterns were practically identical. This would suggest that the third heat treatment was redundant. However, DTA measurements of the same powder after two and three treatments, shown in Fig. 4.2.7, showed a change in the onset temperature of the endothermic peak, from 830 °C after the second to 845 °C after the third heat treatment. This change is significant, because the (optimum) tape sintering temperature was 840 °C. It appears that in the first case, the main DTA peak, located at 885 °C, is accompanied by a shoulder of a second peak, which was marked with an arrow in Fig. 4.2.7. After the third heat treatment, the shoulder has disappeared, while the main peak is still at the same temperature. Instead, the peak at 960 °C has increased slightly. The first endothermic peak possibly stemmed from (partial) melting of the precursor powder [7], even though this has not been proven directly. The DTA peak onset after 4 heat treatments, not shown here, was shifted even further towards higher temperatures, while the XRD pattern again showed no apparent change of the phase assemblage during the fourth heat treatment.

Samples were taken from the powder after two and three heat treatments, respectively, and used to produce PIT tapes. The tape made from powder with only two treatments had zero critical current and very poor microstructure, while the second tape,
with powder made with three treatments, showed good microstructure (shown as tape A in chapter 4.3, Fig. 4.3.6) and superconducting properties (typical $I_c = 24\ \text{A}$, $J_c \approx 12\ \text{kA}$).

XRD measurements of the powders could not clarify the reason for the shifted DTA peaks and contrasting tape properties, and clearly XRD alone was not sufficient for powder characterization. DTA, on contrast, was found to be a powerful characterization tool, because the correlation between the DTA melting onset temperature and the final tape properties was confirmed with several other powders: If the melting in the DTA scan starts at a temperature below the temperature of tape sintering (840 °C), the tape properties will be very poor. This was found to be a very reliable criterion to assess the quality of a powder, even though the DTA measurement is only a very rough simulation of the isothermal tape sintering.

A possible explanation for the DTA criterion is the following: It will be argued in Chapter 4.8 that in tapes, Bi2223 can form both from a liquid, and from a template growth on (solid state) Bi2212. In the latter case, the Bi2212 texture, created through mechanical deformation (Ch. 4.2.3) and recrystallization (Ch. 4.3), will be preserved. A good Bi2223 texture is essential for high critical currents. If, however, Bi2212 dissolves into a liquid, little or no texture will be preserved, and the Bi2223 growing from the liquid will show little if any texture, resulting in poor superconducting properties. DTA indicates the amount of liquid present during tape sintering; if the melting onset temperature is below the tape sintering temperature, there will be abundant liquid, and consequently poor Bi2223 texture and low critical current.

Fig. 4.2.8 shows the microstructure a tape with low melting temperature at the end of the first sintering stage. Bi2212 phase (light grey) is penetrated by Bi2223 needles (dark grey), which have grown randomly in all directions. Large cuprate particles (black) have also formed. In the top left corner, a dark grey particle can be seen, which
according to EDS had the nominal composition of Bi2223, but almost certainly had not a crystalline form. It was possibly a liquid at the tape sintering temperature, although this tape was not quenched.

The question arises, what causes the changing DTA pattern and increased melting, while no apparent change can be seen in XRD measurements. Wang et al. [8] have shown that in their powders lead moves from Ca2PbO4 into Bi2212 during the powder heat treatments, and proposed the lead content in Bi2212 as a main criterion for the ‘state’ of the powder, which they label its ‘maturity’. However, the XRD results shown here (Fig. 4.2.6) show no reduction of Ca2PbO4 or increased lead content in Bi2212, which can be detected through XRD peak width (see chapter 4.3). It is possible that another stoichiometric change occurred in the Bi2212 phase, which remained undetectable by XRD, for example the oxygen content of the Bi2212 phase.
Fig. 4.2.6: XRD scans of a powder after the second and third heat treatment:

- □ = Bi2212, O = (Sr,Ca)2Cu2Oy, CP = Ca2PbO4
Fig. 4.2.7: DTA scans (10 °C/min) of the powder shown in Fig. 4.2.6; after the second and third heat treatment
Fig. 4.2.8: SEM micrograph of a tape after the first heat treatment; made from a powder with low melting point; the silver sheath is at the top (white); Bi2223: dark grey needles; Bi2212: light grey; black: cuprates

DTA measurements were also used to further optimize the temperature for the heat treatment. To avoid formation of Bi2223 and 3221, the sintering temperature had to be chosen between 800 °C and 830 °C. This temperature window was explored by varying the temperature of the second and third heat treatment in a series of powders. The stoichiometry was Bi$_{1.85}$Pb$_{0.35}$Sr$_{1.9}$Ca$_{2.03}$Cu$_{3.05}$O$_{10.1}$X as above, and the heat treatments for all powders are summarized in table 4.2.1. The table also contains the onset temperature of the endothermic peak in the DTA measurement.

Table 4.2.1: Heat treatment of three powders for optimization of sintering temperature

<table>
<thead>
<tr>
<th>Powder No. (internal No)</th>
<th>Heat treatments:</th>
<th>DTA melt onset</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1 (P7B5)</td>
<td>800 °C / 24 h + 800 °C / 12 h + 810 °C / 24 h</td>
<td>825 °C</td>
</tr>
<tr>
<td>P2 (P7B1)</td>
<td>800 °C / 24 h + 810 °C / 12 h + 820 °C / 24 h</td>
<td>845 °C</td>
</tr>
<tr>
<td>P3 (P7B4)</td>
<td>800 °C / 24 h + 820 °C / 12 h + 830 °C / 24 h</td>
<td>825 °C</td>
</tr>
</tbody>
</table>
The highest temperature for onset of melting was found for the second heat treatment schedule, where the temperature was gradually increased with each step. The onset temperatures for the two other powders were increased slightly after a fourth heat treatment, but not above 840 °C. According to the ‘DTA criterion’ stated above, the second heat treatment would be the one preferably used to obtain powders and tapes with highest quality.

4.2.3 Powder Grinding

Grinding of powders was carried out between the calcination steps, in order to improve their homogeneity. A planetary ball mill, with zirconia jar and balls, and an agate mortar and pestle for hand grinding were available. Which of these two methods was used, depended mainly on the amount of powder to be ground. For small batches, hand grinding was preferably used, while for larger batches, the ball mill is more practical. In terms of resulting particle size, both methods were roughly equivalent.

Fig. 4.2.9 shows particle size measurements of a powder in its green (calcined) state, and after 30 and 60 minutes of grinding by hand. The initial powder appeared to have a bi-modal particle size distribution, but from SEM observations (Fig. 4.2.1) it is clear that both of the peaks result from agglomerations of smaller particles. After grinding for 30 - 60 min, the size distribution showed a distribution with three peaks, which was characteristic for powders after grinding. The peak at 20 - 30 μm is again believed to be caused by agglomeration, and the ‘real’ distribution consists of sub-micrometer particles and larger ones in the range of 1 - 10 μm.

The particle size analyzer was equipped with an ultrasonic bath, which was supposed to brake up agglomerations, but in the case of Bi2223 powders, this could not
always be achieved. Apart from this, it is debatable, which is the ‘real’ particle size
distribution and whether the ultrasound should be applied at all. In some cases, the
particle size actually increased after applying ultrasound, and agglomeration was
promoted. Due to these problems, the results obtained with the particle size analyzer
must be treated with caution, although it was always attempted to measure any one
series of powders under identical conditions.

Fig. 4.2.10 shows the particle size distribution of a commercial powder
(Powder ‘B’ in Chapter 4.4) as received, and after 30 and 60 minutes grinding by hand.
In the case of this powder, the peak at 50 \( \mu \text{m} \) first decreased after 30 min of grinding,
but then increased during further grinding. The mean particle size, calculated from the
distribution, also increased from 7 \( \mu \text{m} \) after 30 min to 8 \( \mu \text{m} \) after 60 min. This clearly
demonstrates that the powder particles agglomerated, and the particle size was not
further reduced.

Agglomeration of particles during grinding was also observed directly by SEM,
as shown in Fig. 4.2.11. It was also observed that during the grinding some powders
became sticky and thus difficult to grind, probably by absorption of moisture. This was a
problem particularly during grinding with the planetary ball mill, where the powder
sometimes tended to stick at the side walls. Whether absorption of moisture also caused
the agglomeration, is not clear. In any case, absorption of moisture, and also carbon
dioxide, is undesired. It could be prevented by grinding in vacuum or under an inert gas
atmosphere.

Powder agglomerates were particularly detrimental in multifilamentary tapes, as
shown in Fig. 4.2.12. Here large secondary phases (CuO (black) and Ca\(_2\)PbO\(_4\) (grey) had
formed, but also the filament shapes, even of the adjacent filaments, were distorted.
Fig. 4.2.9: Particle size distribution of an ‘in-house’ powder after the second calcination, and after subsequent grinding by hand for 30 and 60 minutes

Fig. 4.2.10: Particle size distribution of a commercial powder, as received, and after subsequent grinding by hand for 30 and 60 minutes
Fig. 4.2.11: SEM micrograph of a powder with large particle agglomerates on the right-hand side

Fig. 4.2.12: Multifilamentary tape after the second heat treatment, with distorted filaments caused by powder agglomeration
The powder ground as shown in Fig. 4.2.10 was also used to produce a PIT tape. It was found that this tape had zero critical current. This was possibly caused by the formation of an amorphous ‘phase’ during grinding [9], which caused melting at the tape sintering temperature and consequently decomposition of the Bi2212 phase. More interesting in this context is the fact that the texture of the Bi2212 was affected by the reduction in particle size. This was demonstrated by an XRD measurement of the green tape, which is shown in Fig. 4.2.13. XRD patterns of two green tapes are shown, one made with the as-received Merck powder, and the second with the same powder ground for 30 min by hand. The degree of c-axis texture was visible as a reduction of those peaks, which stem from crystal orientations other that the crystallographic c axis. In the second tape in Fig. 4.2.13, these peaks are higher, and thus the degree of c-axis alignment lower. The reduction of the particle size by grinding is undesired in the case of Bi2212, because the size of the platelike Bi2212 crystals determines the degree of texture during the mechanical deformation.

While the formation of an amorphous ‘phase’ could be reversed by an appropriate annealing, the deformation induced texture of Bi2212 is crucial for the texture of Bi2223. After the final powder calcination, the powder must not be subjected to prolonged grinding, to avoid the above effects. A light, brief grinding after the final sintering was found to facilitate the subsequent filling into to the silver tube.
Fig. 4.2.13: XRD spectra of green tapes made with Merck powder as received (A) and ground for 30 min (B); for clarity only Bi2212 peaks are labelled with their Miller indices; the increase in non-00L peaks in B is indicated with arrows.
4.2.4 Powder Contamination

The quality of a Bi2223 precursor powder is very sensitive to impurities of various kinds. The detrimental effects of moisture and CO₂ [10,11,12] were already mentioned in the previous chapter. Of course, these are not only getting absorbed during the grinding, but when the powder is stored in ambient atmosphere. It was observed during this thesis work, that powders which were exposed to air, became sticky, and their properties, when used in PIT tapes, deteriorated. Therefore, Bi2223 precursor powders must be stored in vacuum or an inert gas atmosphere.

It has also been reported that most metallic elements [13] and silicon [12] have a strongly detrimental effect on the powder properties. Contamination during powder handling and storage had to be kept at a minimum. This was of concern especially during grinding, when necessarily a high impact of the grinding media on the powder was required. The materials used were agate and zirconia, and they were generally found to be suitable to avoid contamination. Only in one case, contamination with a zirconia particle was detected in a tape. The SEM micrograph in Fig. 4.2.14. shows that only in the immediate vicinity of the Zr particle, a white secondary phase had formed. Further away from the particle, the Bi2223 formation was not influenced. The tape containing the Zr impurity had been sintered for 35 h at 840 °C, and during this time the zirconia was not dissolved. This finding confirmed that zirconia is an appropriate grinding material for Bi2223 precursor powders, because it does not cause any deterioration on a ‘long’ range.
Fig. 4.2.14: Zirconia particle in a Bi2223 tape after the first sintering stage (35 h at 840 °C)
4.2.5 Summary

The preparation of Bi2223 precursor powders was aimed at achieving a high degree of homogeneity and purity, as well as the desired phase composition and particle size distribution. Spray-drying was shown to be superior to co-decomposition in terms of homogeneity. To avoid the formation of both (Bi,Pb)$_3$Sr$_2$Ca$_2$CuO$_Y$ (‘3221’) and Bi2223, the powder calcination had to be carried out between 800 and 830 °C. The heat treatment sequence was optimized; best results were obtained with 3 - 4 calcination steps and intermediate grinding (GR), which can be summarized as:

\[ 800 \, ^\circ C / 24 \, h + GR + 810 \, ^\circ C / 12 \, h + GR + 820 \, ^\circ C / 24 \, h ( + GR + 820 \, ^\circ C / 24 \, h) \]

XRD and DTA measurements sometimes were inconsistent with each other, as XRD measurements showed little or no difference between different powders, while DTA scans showed large shifts in the melting onset temperature. This onset was found to be a reliable criterion to assess a powder: If the onset temperature of melting was below the tape sintering temperature (usually 840 °C), the tape properties were very poor in terms of microstructure and critical current.

Powder grinding in ambient atmosphere was found to be problematic, as the powder readily absorbed moisture (and probably CO$_2$) during grinding, and became sticky, hindering efficient grinding. It was also observed that the powder particles formed large agglomerates, and consequently a ‘saturation’ in decrease of the particle size was seen. It was shown that prolonged grinding should not be carried out after the final powder calcination. Zirconia and Agate were found to be suitable grinding media.

Future work should concentrate on (i) finding out whether the agglomeration during powder grinding is caused by moisture and (ii) testing if grinding in an inert gas atmosphere or vacuum can improve powder homogeneity.
References


4.3 Atmosphere of Powder Sintering

4.3.1 Introduction

Within the efforts to gain a more comprehensive understanding of the complex chemical phase relations in the Bi2223 system [1-9] and in particular the nature of the Bi2223 phase formation [10-15], the focus has been on the role of the lead, and of the lead containing phases. Typically, a precursor for Bi2223 consists of mainly Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_{8+d}$ (Bi2212) with additional Ca$_2$PbO$_4$, CuO and various Earth Alkaline Cuprates (Sr,Ca)$_x$Cu$_y$O$_z$. Therefore, the lead is shared mainly between Bi2212 and Ca$_2$PbO$_4$. Where the lead resides, depends both on the stoichiometry and the powder processing.

It has been claimed [15,19] that the Bi2223 phase forms in a two step process from Bi2212 through the reactions

\[ \text{Ca}_2\text{PbO}_4 + \text{Bi2212} \Rightarrow \text{Bi(Pb)2212} + \text{SP} \quad (4.3.1) \]

\[ \text{Bi(Pb)2212} + \text{SP} \Rightarrow \text{Bi2223} \quad (4.3.2) \]

('SP' stands for secondary phases) From this it follows that the lead distribution in the precursor, i.e. content of Ca$_2$PbO$_4$ and Bi(Pb)2212 will play a crucial role. Ca$_2$PbO$_4$ is considered as vital, because it provides a liquid phase to speed up the 2223 formation [15,16]. On the other hand, if the Bi2223 phase grows from Bi2212 only if lead is incorporated into Bi2212, the presence of Ca$_2$PbO$_4$ would require an additional, unnecessary step (i.e. reaction (4.3.1)).

Dorris et al. [16,17], and Luo et al. [18] have investigated this problem systematically by mixing powders with variation of lead containing phases Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_{8+d}$ and Ca$_2$PbO$_4$, but constant overall stoichiometry. They found that,
the more Pb is incorporated into 2212, the faster is the conversion into 2223, and the higher is the final critical current density $J_c$ of the tape.

Similar work has been done by Jeremie et al [19]. However, in their work the reactivity of the powder with Pb2212 is slightly reduced compared to their reference ‘standard’ powder (inferred from fig. 4 in [19]), while critical current densities of the tapes were about equal.

Instead of using the ‘two powder process’ [17,20,22] as done in the works discussed above, the Pb can also be ‘shifted’ according to equation (4.3.1) by sintering the powder in a low oxygen atmosphere [21-23]. This is due to the fact that the Pb solubility of Bi2212 increases with decreasing oxygen pressure [24,25].

In the work presented in this chapter, this effect was utilized to produce powders with varying lead distribution, and to compare their performance in Ag sheathed PIT tapes. While it was confirmed that the reactivity of a powder with high amount of Pb-2212 is strongly increased, the critical current density of such a tape was depressed compared to the reference sample. This was attributed to inhibition of Bi2212 recrystallization in the early stages of tape sintering.

4.3.2. Experimental

A Bi(Pb)2223 precursor powder with nominal stoichiometry $\text{Bi}_{1.85}\text{Pb}_{0.35}\text{Sr}_{1.0}\text{Ca}_{2.03}\text{Cu}_{3.05}\text{O}_{10+x}$ was prepared by dissolution of nitrates in nitric acid and solidification in a spray dry machine. The powder was then heat treated at 800 °C for 24 h, ground in an agate mortar, heat treated at 810 °C for 12 h, and again ground. After this step the powder was divided into two batches, which were labelled as powders ‘A’ and ‘B’. Powder A was sintered at 820 °C for 24 h in air, while powder B was sintered in a gas mixture of 1 % oxygen and 99 % nitrogen at 770 °C for 24 h. The lower
calcination temperature in the case of powder B was necessary to avoid formation of Bi2223. It was found that in the 1 % pO2 atmosphere, Bi2223 forms at temperatures as low as 785 °C. Each powder was then ground briefly and filled into a silver tube. The tubes were deformed into tapes with identical deformation schedules. Short (40 mm) samples of the tapes were heat treated in air. Some were ‘quenched’ (50 °C/min) after 1, 10, 20, 35 and 50 h, and investigated by X-ray diffraction and Scanning Electron Microscopy. Other samples were heat treated twice at 840 °C in air for 50 h, with an intermediate ‘sandwich rolling’ [26], and their critical currents (1 µV/cm) determined at 77 K in self field.

4.3.3. Lead Distribution in Precursor Powders

Fig. 4.3.1 shows XRD patterns of precursor powders A and B. The main differences are the suppression of the Ca2PbO4 peaks in powder B, and the width increase of the Bi2212 200/020 peak at 33.0°. The latter indicates that the lead content in the Bi2212 phase had increased during the low pO2 treatment [24]. This was also confirmed with SEM/EDS measurements on Bi2212 crystals in the green tapes, which are shown in Fig. 4.3.2. The EDS analysis was also performed on Bi2212 crystals in tape A after sintering for 20 h, and it was found that indeed the lead content in the Bi2212 phase increased during the tape heat treatment. The XRD scan of powder B in Fig. 4.3.1 also shows an increase in CuO phase. This effect was reproducible and even reversible: after sintering a part of powder B in air, the CuO phase disappeared, and Ca2PbO4 reappeared. There was a interdependence between the formation of cuprate phases and lead containing phases. A similar correlation was found in investigations of stoichiometric variations, which were discussed in chapter 4.1.
Fig. 4.3.1: XRD scans of powders A and B after the final powder heat treatment; □ = Bi2212, O = (Sr,Ca)2Cu2OY, CP = Ca2PbO4

Fig. 4.3.2: EDS measurements from Bi2212 crystals in green tapes A and B, and from tape A after 20 hours sintering at 840 °C
DTA measurements of powders A and B are shown in Fig. 4.3.3. After the second calcination, the melting onset was at 830 °C, and after the third calcination it was increased to 845 for powder A, and slightly higher to 850 °C for powder B. The difference between the two powders is insignificant. This result contradicts the findings of Huang et al. [7], who claimed that the presence of Ca_2PbO_4 (such as in powder A) is responsible for the formation of a liquid phase. In our powders, the presence or absence of Ca_2PbO_4 did not influence the onset temperature of the melting.

Fig. 4.3.3: DTA scans (10 °C/min) of powders A and B after two and three calcinations
4.3.4 Bi2223 Formation Rate, Microstructure and Critical Currents

The phase evolution during tape sintering was examined by XRD, as shown in Fig.s 4.3.4. and 4.3.5. While in tape A (from powder A) the Bi2223 formation commenced only after 20 hours, in tape B (containing powder B) Bi2223 was observed after just 1 hour of sintering, and the transformation into Bi2223 was essentially complete after 35 h. The EDS and XRD results strongly suggest that the Bi2223 formation indeed followed the sequence Bi2212 → BiPb2212 → Bi2223 (equations (4.3.1) and (4.3.2)), and that the reactivity in powder/tape B is much higher, because the first step has been 'pre-empted' during the low pO2 heat treatment.

However, the final critical currents of samples from powder/tape B were only around half of those from tape A (typically $I_c(A) = 24$ A, $I_c(B) = 14$ A).

SEM micrographs of samples from tapes A and B, quenched after various times, are shown in Fig. 4.3.6. In the green tapes (first row in fig. 4.3.6), the microstructure and the initial particle size of the Bi2212 phase (light grey) was similar in both tapes. After 1 h sintering (second row), the Bi2212 grains had recrystallized in both tapes. The third row in Fig. 4.3.6 shows that after 10 h the Bi2212 grain size has further increased in tape A, while in tape B Bi2223 phase (dark grey needles) had appeared. After 20 h (row #4 in Fig. 4.3.6), the first Bi2223 crystals appeared in tape A (indicated with white arrow) while the Bi2212 grains had further recrystallized. In tape B, on the contrary, the Bi2212 phase was not recrystallized, but further transformed into Bi2223. The microstructure of both tapes at the end of the first sintering (50 h) is shown in the last row of Fig. 4.3.6. While there was still some Bi2212 (light gray) present in tape A, Bi2223 (dark grey) was predominant in both tapes. The Bi2223 grains, however, were significantly larger (longer and thicker) in tape A. (Note that all micrographs shown in Fig. 4.3.6 were taken with the same magnification). This is the reason for the much
higher critical currents found in tape A, as the number of grain boundaries is largely reduced.

Thurston et al [27] and Frello et al. [28,29] performed transmission XRD measurements of tapes. They found that the Bi2212 phase was realigning (with c-axis along the tape) during early sintering stages, and the Bi2223 phase formation started after an initial ‘delay period’, very similar to tape A of this work. In tape B, in contrast, the Bi2212 recrystallization was inhibited, probably due to the Bi2223 growth.

The ‘better’ Bi2212 morphology (i.e. larger Bi2212 grains with higher degree of alignment) of tape A lead to a better Bi2223 morphology. This argument implicitly assumes that the Bi2223 formation was governed by a direct growth on Bi2212 ‘templates’. In Chapter 4.8.2 direct evidence will be shown for this growth model.

The main conclusion is, that the initial ‘delay’ of Bi2223 formation, probably due to reaction (4.3.1), is beneficial, because it allows the regrowth and alignment of the Bi2212, leading to an improved Bi2223 morphology.
Fig. 4.3.4: XRD patterns of samples from tapes A and B sintered for various times; □ = Bi2212, ▽ = Bi2223, Δ = Bi2201
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Fig. 4.3.5: Bi2223 formation rate; calculated from data in Fig. 4.3.4; expressed as ratio of Bi2223(0010) and Bi2212(008) XRD peak heights $h_{2223}/(h_{2223}+h_{2212})$

NEXT PAGE:

Fig. 4.3.6: SEM micrographs (all with magn.10k) of samples from tapes A and B sintered for various times; light grey = Bi2212, dark grey needles = Bi2223, black grains = Sr$_x$Ca$_y$Cu$_z$O$_d$ or CuO
CHAPTER 4.3: ATMOSPHERE OF POWDER SINTERING

Tape A  

Tape B  

sintering time

0 h

1 h

10 h

20 h

50 h
4.3.5. Summary

While it was confirmed that

- the Bi2223 formation is probably governed by a two-stage sequence
  \[ \text{Bi2212} \rightarrow \text{BiPb2212} \rightarrow \text{Bi2223} \]

and

- sintering a Bi2223 precursor powder in a low oxygen partial pressure strongly
  increases its reactivity, due to the increase of Pb-rich Bi2212,

it was also found that

- a higher reactivity of the precursor not necessarily leads to a higher critical current of
  the final tape,

because

- an initial delay in Bi2223 formation is beneficial in allowing the regrowth and
  realignment of the Bi2212 grains

and

- the Bi2212 morphology in the tape determines the final Bi2223 morphology.
CHAPTER 4.3: ATMOSPHERE OF POWDER SINTERING

References

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    321
    1835


4.4 External Powder Sources

4.4.1 Introduction

While the commercial market for High Temperature Superconductors grows, the production of Bi2223 precursor powders in reproducible quality and large quantities is a difficult task. Bi2223 precursor powders have become a commodity, and can be purchased from a number of chemical companies.

The production of powders during this thesis work, which was described in the previous chapters, was confined to small batches of 10 - 50 g. It was found that upgrading the production to larger quantities is not possible without acquisition of appropriate equipment and know-how. On the other hand, when considering production of long-length tapes, powder in sufficient quantity and quality has to be available. Testing of powders from external sources is therefore a crucial part of application-oriented research on Bi2223 PIT tapes. It is also useful to test ‘home-made’ precursor powders against commercial products as a benchmark.

4.4.2 Experimental Details

Three powders from different sources were tested. The powders will be labelled A, B and C, and their known specifications are summarized in Table 1.

Table 4.4.1: Supplier, Cation stoichiometry and production method of powders A, B and C

<table>
<thead>
<tr>
<th>Powder #</th>
<th>Source</th>
<th>nom. Stoichiometry</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Queensland University</td>
<td>?</td>
<td>co-precipitation</td>
</tr>
<tr>
<td>B</td>
<td>Merck Ltd., UK</td>
<td>Bi_{1.85}Pb_{0.35}Sr_{1.95}Ca_{2.05}Cu_{3.06}O_x</td>
<td>spray pyrolysis</td>
</tr>
<tr>
<td>C</td>
<td>Superconducting Components Inc.</td>
<td>Bi_{1.84}Pb_{0.34}Sr_{1.91}Ca_{2.03}Cu_{3.06}O_x</td>
<td>?</td>
</tr>
</tbody>
</table>
The powders were filled into silver tubes with 6.5 mm diameter, and then drawn and rolled into monofilament tapes of 250 μm x 3 mm. Short samples were heat treated at 840 °C for 40 h in air, then rolled to 200 μm, and again heat treated, this time with a two step process (see Chapter 4.7), with 30 h at 840 °C and 40 h at 820 °C. Other tapes were only heat treated once for shorter times and then fast cooled. The tapes were investigated by XRD, SEM, and critical current measurements.

4.4.3 Microstructure and Critical Currents

Fig. 4.4.1 shows SEM micrographs of tapes made from powders A, B and C, after the first heat treatment. The morphologies of tapes/powders A and B were found to be quite similar, but they were clearly different to that of powder C. The main difference was the particle size of the Bi2223 phase (visible as dark grey needles), which was much larger in tapes A and B. One can also see some large Bi2212 crystals (light grey) in these tapes. This is quite remarkable; it means that some Bi2212 grains had not been transformed into Bi2223, but recrystallized into very large grains. This is a typical, if little understood, phenomenon in sintered ceramics, and referred to as "exaggerated grain growth" [1]. Apparently, Bi2212 phase is stable to some extent and can co-exist with Bi2223 at 840 °C. In contrast, no Bi2212 phase was found in the micrograph of tape C, but some CuO and Bi2201 appeared as secondary phases. In all three samples the Bi2223 grain alignment was rather poor.

The final microstructure after intermediate deformation and second sintering stage is shown in Fig. 4.4.2. The microstructure of tape C (from powder C) again showed distinctive differences from the other two samples. One can see again that the Bi2223 grain size was much smaller in tape C, but furthermore, this tape now showed a large amount of secondary phases, especially Bi2212, visible as long, light grey needles.
CHAPTER 4.4: EXTERNAL POWDER SOURCES

There were also large particles of CuO (black) and (Ca,Sr)\(_2\)PbO\(_4\) (light grey) present. Tapes A and B contained much less secondary phases. In tape A, but not in B, large (Ca,Sr)\(_2\)PbO\(_4\) were found. Both tapes contain smaller amounts of CuO and Bi\(_{2212}\).

The critical currents after the second sintering stage were 29 A for tape A, 27 A for tape B and 9 A for tape C. These results can be attributed to the differences in the microstructure. The smaller Bi\(_{2223}\) grain size in tape C means, that a superconducting current has to pass more grain boundaries, i. e. weak links, per unit length. The larger amount of secondary phases reduces the superconducting volume and therefore the number of current paths.

It was also attempted to improve the critical current especially of tape C by varying sintering temperature and time, but no increase in critical current was found.

4.4.4 Bi\(_{2223}\) Formation Speed and Stability

In order to investigate the reactivity of the powders, some tapes were sintered for shorter times and then fast cooled. The phase assemblage was investigated by XRD measurements. Fig. 4.4.3. shows the phase composition after 1 hour, 10 hours, 40 hours (at the end of the first heat treatment) and after the second heat treatment. After one hour, only Bi\(_{2212}\) peaks were detected in the scans of tapes/powders A and B, but in tape C both Bi\(_{2212}\) and Bi\(_{2223}\) peaks were present with the same intensity, indicating that the transformation from Bi\(_{2212}\) into Bi\(_{2223}\) occurred at a very high rate in this tape. After 10 h, the Bi\(_{2223}\) formation had only started in powder A, but Bi\(_{2223}\) peaks were higher than Bi\(_{2212}\) in powder B, e. g. the ‘reactivity’ was higher in powder B compared to A. The XRD scans taken at the end of the first and second heat treatment (third and forth row in fig. 4.4.3) confirmed the microstructural observations with SEM. In tape C Bi\(_{2212}\) regrew at a high rate during the second, two-step sintering, while in
powders/tapes A and B only small amounts of Bi2212 were present. There was a difference between powder C and the other two not only in ‘reactivity’, but also in Bi2223 phase stability. The Bi2223 phase was formed faster at 840 °C, but also decomposed faster at 820 °C in tapes from powder C.
Fig. 4.4.1: SEM (backscattering) micrographs of tapes from powders A, B and C after the first sintering stage (40 h at 840 °C); matrix (grey needles) is Bi2223
Fig. 4.4.2: SEM (backscattering) micrographs of tapes from powders A, B and C after the second sintering stage
Fig. 4.4.3: XRD scans of tapes made from powders A, B and C, after 1, 10 and 40 h and after the second heat treatment; ▽=Bi2223; □=Bi2212
4.4.5 Conclusions and Summary

The comparison of three external powders in this chapter has confirmed the results of studying two 'home-made' powders in Chapter 4.3: There was an inverse relationship between the reactivity during tape sintering and the Bi2223 grain size, and the critical current density increased with increasing grain size. The comparison in this chapter also indicated that there might be an inverse correlation between the reactivity and the Bi2223 phase stability.

Table 4.4.1 shows that the stoichiometries of powders B and C were almost identical. Therefore the stoichiometry is unlikely to be the cause of the very different characteristics in tape morphology. While the details of the powder processing for these powders were unknown, this study showed that different production processes lead to very different morphologies and particle sizes, which in turn resulted in large variation of superconducting properties.

References

4.5 Addition of Silver Particles to the Core

4.5.1 Introduction: Influence of silver on Bi2223 phase formation and texture

It has been established that in Ag sheathed Bi2223 and Bi2212 tapes the silver clad is not only useful as a mechanical and chemical protection of the superconducting core, but also plays an important role in the phase development and grain alignment of the superconducting phase during the sintering. Detailed microstructural studies [1-3,23] show that along the interface both Bi2212 and Bi2223 grow with a high degree of texture and phase purity, which is desirable for high critical current densities. Fig. 4.5.1 shows the interface region of a Bi2223 tape after the final heat treatment. Along the silver, one can see Bi2223 grains with ‘perfect’ texturing and no secondary phases.

Fig. 4.5.1 Core-sheath interface of a Bi2223 tape; the silver sheath is at the top of the photo (light grey area)
It appears that along the core - Ag sheath interface, Bi2223 preferably grows parallel to the interface. This could be caused by wetting of the interface by a liquid phase. To test this hypothesis, DTA measurements were carried out to simulate the phase formation. Fig. 4.5.2 shows a comparison of DTA scans, of a Bi2223 precursor by itself, and then mixed with a silver powder. As a result of the silver addition, the melting onset temperature dropped from 865 to 810 °C, which is well below the tape sintering temperature of 840 °C. Although DTA (in air) is only a very rough simulation of the isothermal sintering (in a tape), it can be concluded that during tape sintering, much more liquid phase is formed close to the silver interface compared to the bulk core. Most likely, this has important consequences on the Bi2223 formation (see Chapter 4.8). From a technological point of view, the silver-core interface certainly has a beneficial effect, promoting Bi2223 texture and phase purity. It is therefore desirable to maximize the interface area. Multifilamentary tapes have a number of advantages over mono-core tapes; one of them is the increased silver-core interface. Fig. 4.5.3 shows a comparison of critical current densities in Bi2223 tapes from various commercial suppliers, plotted as function of the number of filaments. The current density increases with the number of filaments, demonstrating the importance of the silver-core interface. Consequently, the morphology of the interface is crucial for the tape properties. This topic, and the importance of appropriate mechanical deformation, are discussed separately in Chapter 4.6.
Fig. 4.5.2: DTA scans of a Bi2223 powder a) by itself and b) mixed with 25 wt% silver powder

Fig. 4.5.3: Critical Current Densities in commercial Bi2223 tapes (length > 100 m; data from suppliers; as of July 1997)
Due to the facts discussed above, it is reasonable to suppose that silver added to the core would improve the critical current density of Bi2223/Ag tapes, because it would provide an additional ‘interface’. The effect of silver additions in Bi2223 tapes has been investigated in several studies [2,4-8]. The results were somewhat contradictory, but it was generally found that the addition did not significantly improve the properties of the tapes.

In this work it is shown that the particle size of the silver particles added is a most important factor, and that addition of large silver particles strongly improves the critical current, in particular of ‘thick’ (300 μm) Bi2223/Ag tapes, which are being used for current leads. The motivation to produce ‘thick’ tapes is as follows. When using silver-sheathed HTSC tapes as a current lead component [9,10], as was done in this thesis (Chapter 5), it is desirable to minimize the thickness of the silver sheath, to minimize the thermal conductivity [11]. The optimum tape thickness in terms of critical current density is around 100 μm [12], but a tape with a thin silver sheath cannot be rolled to this thickness, because the sheath tends to crack, esp. in alloyed silver which is preferably used for current lead tapes [9,13,14].

4.5.2 Experimental Details

Bi2223 PIT tapes were made using silver tubes with an outer diameter of 6.5 mm and wall thickness of 0.5 mm. BiPbSrCaCuO(2223) precursor powder was mixed with two different silver powders. The particle size distribution of the silver powders and the Bi2223 precursor powder is shown in Fig. 4.5.4. The fine silver powder was purchased from a commercial source, with specification of average particle size given as 5 μm. The average particle size derived from the measurement shown in Fig. 4.5.4, however, was 25 μm. The coarse powder was produced by filing a silver rod. Its average particle size
was 225 μm. Tapes with four silver ratios of 0, 10, 25 and 40 wt% of the coarse silver, and a tape with 25 wt% of fine silver powder were made.

The filled tubes were form rolled and rolled, and the final tapes had a cross-sectional area of 360 μm x 3 mm. The cross-sectional core-sheath ratio was around 50 - 50 % (compared to about 25 - 75 % for 'usual' tapes). 40 mm - 400 mm pieces were sintered at 842 °C for 35 h in air, then 'sandwich rolled' [15] to 300 μm and again sintered in air (25 h at 842 °C + 50 h at 825 °C).

Chemical and microstructural characterization was carried out by Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD), and electromagnetic properties were investigated through measurement of critical currents at 77 K in self-magnetic field and external fields.

4.5.3 Effects of silver addition

I. Microstructure

Fig. 4.5.5 shows XRD patterns of three tapes with 25 wt% coarse, 25 wt% fine and 0% silver, after the final heat treatment. In all cases Bi2223 was found as the major phase, with small amounts of Bi2212 and some silver present. The tape containing fine silver powder appeared to have a larger amount of residual Bi2212 phase, and the (019) peak of the Bi2223 phase was slightly higher in the scan of the tape without silver addition. This can be interpreted as a lower degree of texture in this tape. However, the differences between the XRD patterns were rather subtle. This is due to the fact that the XRD samples were prepared by peeling off the silver sheath, i.e. the superconducting core along the core-sheath interface was always measured, which in general is not representative for the bulk superconductor [16,17,23].
Fig. 4.5.4: Particle size distribution of the silver powders and the Bi2223 precursor powder (Merck (UK) Ltd.)
Fig. 4.5.5: XRD patterns of Bi2223 tapes with addition of 25 wt% 'coarse' Ag, 25 wt% 'fine' Ag, and without Ag addition; after the final heat treatment; \( \nabla = \text{Bi2223}, \square = \text{Bi2212} \)
SEM allowed a more direct observation of the microstructure. Fig.s 4.5.6, 4.5.7 and 4.5.8 show longitudinal cross sections of tapes after the final heat treatment, with 0%, 40wt% coarse, and 25wt% fine silver powder, respectively. The Bi2223 grains in the core without silver (Fig 4.5.6 a,b) had a rather low density and were not well aligned, resulting in many high angle grain boundaries. Some large secondary phases (Bi2212, SrCaCuO and CuO) were present.

When large silver particles had been added to the core (Fig. 4.5.7 a,b,c), these were squeezed into long flat layers during the deformation by rolling. Along the silver layers the Bi2223 phase was well aligned and had a high density, with fewer secondary phase particles. The beneficial effect of the silver addition is particularly evident in Fig. 4.5.7 c, between the Ag ribbons, where the Bi2223 phase has formed with very high texture, density and purity. This microstructure is favourable for a high superconducting critical current.

Fig. 4.5.8 is the microstructure of a tape with small silver particles in the core. Obviously, these did not improve the grain alignment compared to the tape in Fig. 4.5.6, and an increased amount of secondary phases was found, in particular more Bi2212 phase (light grey needles). It can also be seen that the silver particles had a rather wide size distribution, but only some short silver ribbons had formed. This demonstrated that the silver particle size is an important factor determining the effect of the silver addition.
Fig. 4.5.6 a,b: SEM micrographs of a tape without silver addition, after the final heat treatment; dark grey needles: Bi2223, light grey needles: Bi2212; light grey round particles: Ca2PbO4, black: cuprates
Fig. 4.5.7 a,b: SEM micrographs of a tape with addition of 40 w% coarse silver, after the final heat treatment; white ribbons: Ag, grey needles: Bi2223; black: cuprates
Fig. 4.5.7 c: SEM micrograph of a tape with 40 w% coarse silver, after the final heat treatment; white ribbons: Ag, grey needles: Bi2223, black: cuprates

Fig. 4.5.8: SEM micrographs of a tape with addition of 25 w% fine silver, after the final heat treatment; white: Ag, dark grey needles: Bi2223, light grey needles: Bi2212; light grey round particles: Ca$_2$PbO$_4$, black: cuprates
II. Superconducting properties

The differences in the microstructures were reflected in the superconducting properties. Fig. 4.5.9 shows critical currents of tapes against silver content in the core, in self field at 77 K. Each data point and bar represents the average and standard deviation of 14 measurements, taken from 1 cm pieces of several 10 cm long tapes. Critical currents of tapes without silver were around 30 Amperes, or current densities of 6000 A/cm². This result fitted well with the findings of Grasso et al.[12], who have systematically investigated $J_c$ as a function of core thickness. The addition of coarse silver powder led to a strong increase in $I_c$, and the highest values were found in tapes with 25 wt% Ag. In contrast, the addition of 25 wt% fine silver powder to the core led to a slight reduction of the critical current, probably due to the increased amount of secondary phases.

The increased length of the error bar in tapes with Ag addition indicates that the deviation of the critical current, i.e. the inhomogeneity of the tape, increased in tapes with addition of coarse Ag powder. This can also be seen in the variation of local $J_c$ (1 cm pieces) in a 40 cm long tape, which is shown in Fig. 4.5.10. This can be attributed to an inhomogeneous distribution of the silver particles. The silver and Bi2223 precursor powders for the tapes described here were only mixed by hand, and an improved technology for mixing and filling the powders has to be found.

Some results of $J_c$ measurements of short tapes (4 cm) in magnetic field are shown in Fig. 4.5.11. For the best short tapes the improvement of $J_c$ due to the silver additions was up to 60% in self field, and even larger in external magnetic fields. The inset to Fig. 4.5.11 shows the ratios of $I_c$'s in 100 mT and in self field, and this ratio is improved from 20% to 30%. This meant that the number of 'strong links' had been increased [18,19], or in other words, that the number of 'active current paths' in...
magnetic field was much higher[20]. One has to consider that the self field of a tape with 3.5 mm width and 50 A was already around 8 mT [21].

Fig. 4.5.9: Critical Currents vs. silver content for ‘coarse’(□) and ‘fine’(O) Ag powder; each data point is the average, and each bar the standard deviation of 14 measurements from different samples (1 μV / 1 cm)

Fig. 4.5.10: Critical current (1 μV / 1 cm) against position in a 40 cm long tape with 25 wt% silver addition
Apart from the increased inhomogeneity in silver 'doped' tapes which was discussed above, it was found that in these tapes the critical currents were generally higher in short samples (4 cm) compared to longer tapes (10 - 40 cm, see Figs 4.5.9-11), although the production process was identical (in particular no pressing was used for short tapes). Such a difference was not found in the reference tapes without silver addition.

The reason for this difference could have been some imperfection of the Bi2223 precursor powder, e.g. residual CO₂ or moisture, or its oxygenation state, which led to a reduction of $I_c$ in the long tapes. This indicated that in the silver-'doped' case $I_c$ was...
limited by the 2223 powder properties, and not any more by the grain texture and connectivity. Thus a further increase of critical currents by improvements of powder properties can be expected.

III. Ag addition and ‘Sausaging’

As the large silver particles are deformed into long ribbons, their final shape depends critically on the deformation schedule. Similar to the core-sheath interface, they can suffer from a ‘sausaging effect’, which is discussed in Chapter 4.6. In fact, during the rolling this effect occurs at an earlier stage at the silver layers, and the silver addition can be used as a tracer of the powder flow [22]. However, in this work it was found that they could not prevent the formation of sausaging, as was claimed by Zhou et al. [6], because in the late rolling stages the silver was much softer than the oxide powder.

4.5.4 Magnetization Measurements

Magnetization measurements were carried on a number of samples, in order to investigate superconducting properties at temperatures below 77K. Fig.s 4.5.12 a, b and c show the magnetic moment M as function of magnetic fields H up to 5 T, at 5K, 20 K and 77K, respectively. Each plot shows results from a sample with addition of 25 w% coarse silver, and a reference sample without silver addition. At 5 K and 20 K, a crossover was observed between the M(H) curves of the two samples. The cross over field was around 2 Tesla for both temperatures. According to the Bean model [24,25], the magnetization is proportional to the critical current of the superconductor, and consequently, there is also a crossover in the critical currents of the two samples. While at magnetic fields below 2 Tesla, the critical current is higher in the sample with silver addition, at higher fields it is higher in the reference sample without silver added to the
core, up to a factor of 2 at 5 Tesla. As the magnetic properties of a superconductor in such high fields is dominated by flux pinning [25], it follows that the sample without silver addition has better flux pinning properties at low temperatures and high fields. While Bi2223 grains grown along a silver interface show near-perfect texture and phase purity on a micrometer scale, they may also have a higher degree of perfection in their crystal structure on an atomic scale. A reduction of crystal defects probably results in a reduced intrinsic pinning in Bi2223, as was found in other HTS [29]. Furthermore, non-superconducting areas at grain boundaries with misorientation, which also contribute to the pinning [30], are probably reduced in tapes with silver addition.

At 77 K, no crossover was found, because at this temperature the width of the magnetization loop decreases to zero at around 200 mT, which is far smaller than the crossover field. From the M(H, 77K) data, the critical current was calculated with the Bean formula [24-28]

\[ J_c = 30 \frac{\Delta M}{d \cdot V}, \]

where \( \Delta M \) is the width of the magnetization loop (in emu), \( d \) is the width of the sample (in mm) and \( V \) the volume of the sample (in mm\(^3\)). The pre-factor 30 is a demagnetization factor for a square-shaped sample [26,27]. The data are shown in Fig. 4.5.12d, together with the transport measurement. The transport and magnetic data coincide in zero field, but they are very different in applied magnetic field. The magnetization loop is a much more sensitive measure of the electric field in the sample compared to the transport measurement, where an arbitrary criterion of 1 \( \mu \text{V/cm} \) is commonly chosen [26].
Fig. 4.5.12 a,b: Magnetization loops of samples with and without silver addition, at 5 and 20 K
Fig. 4.5.12 c: Magnetization loops of samples with and without silver addition, at 77 K

Fig. 4.5.12 d: Critical current densities from transport measurements (Fig.4.5.11) and as calculated from magnetization measurement (Fig.4.5.12 c)
4.5.5 Summary

The effect of silver additions on the microstructure and superconducting properties of \((\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x\) (Bi2223)/Ag tapes has been investigated. Critical currents were found to depend both on the silver content and especially the silver particle size. The addition of small (5 \(\mu\)m) particles resulted in a slight reduction of the critical current. Large (400 \(\mu\)m) particles were squeezed into long flat layers, leading to better grain alignment, grain density and phase purity of the 2223 phase along these layers. As a consequence, the critical current was increased by up to 60 \% in self magnetic field, and even more in an external magnetic field. Magnetization measurements revealed that the critical current at low temperatures (5 - 20 K) and high magnetic fields (> 2 Tesla) was lower in samples with silver addition.

References

CHAPTER 4.5: ADDITION OF SILVER PARTICLES TO THE CORE


4.6 Mechanical Deformation of Tapes; Sausaging

4.6.1 Introduction

The mechanical deformation of the filled silver tubes into flat, flexible tapes is of great importance. It strongly influences the final density and texture of the core powder, as well as the smoothness of the core-sheath interface, which in turn are major factors determining the superconducting properties. This chapter focuses on the problem of distortion of the silver-core interface which can develop during the rolling sequence, as shown in Fig. 4.6.1. This 'sausaging' effect leads to a reduced effective current path and, more seriously, disturbs the desired texture of the BiSrCaCuO grains [1].

Generally, 'sausaging' is a consequence of the very different mechanical properties of the components of the composite structure. But a detailed theoretical understanding of the rolling process and the distortion is very difficult, due to the complexity of the deformation and the large number of operation parameters. From these the relevant parameters have to be extracted which determine the result.

4.6.2 Tape Geometry And Density Measurements

For some tapes, the width and length increase during the deformation was measured, as displayed in Fig 4.6.2. The 'direction' of the strain was found to be a function of several deformation parameters, e.g. increasing the roller speed, roller diameter or reduction rate resulted in an increased width strain and decreased length strain (wider and shorter tape). However, it was found that in no case the width strain became zero, and the deformation was always three-dimensional. This has to be kept in mind when using textbooks on rolling of metals, where the deformation is usually treated as a two-dimensional process.
Fig. 4.6.1: Development of 'sausaging in a monofilamentary tape during rolling; a) thickness 250 \( \mu \text{m} \), b) 160 \( \mu \text{m} \), c) 105 \( \mu \text{m} \).

Fig. 4.6.2: Relative width increase and volume decrease during flat rolling of a Bi2223/Ag tape.
The measurement of tape geometry allowed a direct and rather accurate
determination of density changes. The surprising result was, that after an initial
compression in the early rolling passes (down to ca. 1mm thickness), the volume of the
tape remained constant. Independantly of the rolling parameters the density was not
further increased below 1mm thickness. This thickness was much larger than the ‘onset
thickness’ of sausaging in all tapes. For example, in the tape shown in Fig. 4.1.1 no
sausaging was seen at 250 μm thickness. Similar results have been found by
Korzekwa et al. [4].

These results are contradicting the theoretical model of Han and Freltoft [1], who
described the core oxide powder and its deformation in terms of a ‘flow model’, the
crucial parameter being the powder density. According to their model, when the density
reaches a critical value, powder flow along the rolling direction is inhibited and
‘sausaging’ occurs. The results shown here indicate that the macroscopic powder density
is not the critical parameter. A density fluctuation on a microscopic scale, however,
might be involved in sausaging formation.

4.6.3 Tracing The Powder Flow with Silver Addition

When large silver particles are added to the BiSSCO powder, these are squeezed
during the deformation into long flat layers. Optimization of the the rolling parameters
and the size of the silver particles enhances the texture of the BiSCCO grains and
reduces the sintering time, as was shown in Chapter 4.5.

For this study, very soft (i.e. well annealed) silver particles were mixed to the
precursor powder in order to mark out the powder flow. Fig. 4.6.3 shows that the silver
layers were deformed in a wavy shape. This phenomenon was also observed at a ‘large’
thickness of 0.6 mm, when no sausaging occured at the core-sheath interface. It can also
be seen that the wavy powder flow was not confined to the interface region, but is a phenomenon of the entire, bulk core. Silver addition could be a very powerful tool to optimize the deformation, as these tentative results demonstrate.

Fig. 4.6.3: Bi2223/Ag tape with silver particle addition to the core

4.6.4 Sausaging, Shear Bands and Necking

From the observations in the previous chapter it has to be concluded that the non-uniform, wavy powder flow is an 'intrinsic' dynamical property of the powder transport, i.e. it is not confined to the core-sheath interface. This important conclusion is further confirmed by the observation that in multifilamentary tapes the distortion reached across several filaments, as shown in Fig. 4.6.4. It can be seen that the distortion appeared as zig-zag lines across the tape. In monofilamentary tapes, a similar distortion appeared as a crack pattern. Fig. 4.6.5. shows a tape where a zig-zag crack pattern was visible even after the first sintering stage. More often, arrays of very small cracks were found in green tapes, as shown in Fig. 4.6.6a, which were then overgrown during tape sintering. The result was a wavy ‘discontinuity’ of the grain texture, such as in Fig. 4.6.6b. Therefore,
even small, overgrown cracks cause grain misalignment, and therefore most likely result in decrease in critical current.

Fig. 4.6.4: Sausaging in a multifilament tape; the distortions form a continuous zig-zag line across the entire tape

Fig. 4.6.5: Monofilamentary tape after the first sintering, with an array of shear cracks through the core
Fig. 4.6.6 a: Crack pattern in a green monofilamentary tape

Fig. 4.6.6b: Microstructure of a monofilamentary tape after the first sintering stage; (rolling direction = left-right); the 'discontinuity of the grain texture (marked with arrows) is believed to be caused by a shear crack
In flat rolling of metals, similar line patterns form too, and they are commonly known as shear bands. Fig. 4.6.7 shows an example. Shear bands in metals form when the deformation strain exceeds a critical value of the material [2][3][13]. They can cause shear cracks, as shown in Fig. 4.6.8. These crack patterns look very similar to those found in HTS tapes (Fig.s 4.6.4, 4.6.5), and therefore it can be stated with certainty that the cracks and distortions in HTS tapes are the result of shear band formation. In particular, the distortion of the core-sheath interface, i.e. ‘sausaging’, is a consequence of shear band formation. To further verify this hypothesis, another analogy in metal forming may be considered. Shear bands form not only during rolling of metals, but also other types of deformation. Fig. 4.6.9 shows a metallic workpiece after a tensile test. Here the formation of shear bands is accompanied by necking of the workpiece. Necking is a very common (and usually undesired) phenomenon especially in sheet metal forming [4][5]. In analogy, the formation of sausaging in Ag-sheathed HTS tapes can be regarded as necking of the filaments.

However, while the experimental similarities are remarkable, great caution is necessary when adopting the classical theory of plastic deformation of metals to the deformation of the oxide powder. The shear band formation in metals is related to accumulation of dislocations in their atomic structure. In the oxide powder considered here, the microscopic origin of the shear bands is unclear.

The correlation between sausaging and shear band formation has been shown very convincingly in a paper by Kautz et al. [6]. However, they claim that shear bands in the silver sheath cause sausaging, which is inconsistent with their own experimental results (they find increased formation of sausaging with increased frequency of annealing during deformation). The formation of shear cracks, in particular the crack orientation, is discussed very detailed by Korzekwa et al. [7] and Han et al. [8].
Fig. 4.6.7: Shear bands in rolled Copper (60 % reduction, rolling axis = micron bar) 
(from Ref [13])

Fig. 4.6.8: Rolling failures in a) magnesium and b) brass (from Ref. [2])

Fig. 4.6.9: a) Necking and shear band formation in Al-Cu tensile test sample(from [4])
    b) shear fracture in a Niobium tensile test sample (from [4])
4.6.5 Parameter study

A large series of Ag-sheathed Bi2223 tapes, prepared by the ‘Powder-in-Tube’ method, were rolled from 2 mm to 0.2 - 0.1 mm with variation of roller diameter, roller speed, reduction rate, intermediate annealings (temperature and frequency), powder particle size, initial interface smoothness, initial diameter and thickness of the silver tube. Each parameter was varied with the others being kept constant. Samples were taken at various steps of deformation to monitor the onset of ‘sausaging’. By using optical microscopy the distortion was qualitatively assessed and compared.

Two roller diameters (234 mm and 55 mm) were compared. The use of the large roller diameter resulted in a better interface quality, as shown in Fig. 4.6.10 a and b. This result is consistent with a recent publication by Wang et al. [9], who developed a new method called ‘sandwich rolling’, where the superconductor tape is rolled between two steel tapes. This process is equivalent to the use of a very large roller diameter and results in a very smooth interface. The result of this work is in contradiction to that of Korzekwa et al. [7] who find that a smaller roller yields a less distorted interface. Fischer et al. [15] and Kovac et al. [16] both found higher critical currents in tapes rolled with large roller diameter compared to smaller ones, but they did not report on the interface morphology.

A comparison of deformation with different rolling speeds (4 cm/sec and 6 cm/sec) showed that a small rolling speed is favourable to avoid sausaging (Fig 4.6.10 a and c). The formation of sausaging depends strongly on the thickness reduction rate, as shown in Fig 4.6.10 a and d. The thickness reduction per pass has to be chosen below a ‘critical’ value which decreases with decreasing tape thickness (e.g. 30% to 0.8 mm, 15% to 0.4 mm, 10% below 0.4 mm - but these values depend on the other parameters too).
Intermediate annealing of the tapes has to be carried out to some extent to avoid cracking of the silver sheath. Not surprisingly, it was found that both temperature and frequency of these annealings must be kept as low as possible to minimize the interface distortion.

Also investigated was the influence of the initial geometry and other properties of the tape itself, including initial smoothness of the interface, powder particle size,
sheath-core ratio (i.e. tube wall thickness) and initial diameter (resulting in different final tape widths). It was found that these parameters apparently are not relevant to the formation of sausaging.

4.6.6 Discussion and Theoretical Considerations

The most remarkable result of the parameter study was the dependence of the sausaging on the rolling speed. This parameter is distinguished because it involves time as a variable. The deformation has to be considered as a time-dependant, non-equilibrium process. A similar behaviour is also known from the plastic deformation of metals [10], as will be discussed later.

One could say that the deformation has to be carried out sufficiently slowly in order to allow the powder flow along the tape direction. This can be expressed mathematically by assuming that the process time \( t_p \) has to be larger than a hypothetical relaxation time \( t_r \) of the powder. If \( t_p \) is smaller than \( t_r \), the powder flow is disturbed or inhibited, which results in the formation of sausaging. The relaxation time is a complicated function of the powder properties and the geometry, and can not be given explicitly. However, by assuming its existence and deriving the process time \( t_p \), some conclusions can be drawn from this concept.

![Fig. 4.6.11: Geometry of the rolling gap](image-url)
From Fig 4.6.11 it can be seen that

\[ \alpha = \frac{a}{d/2} \quad (4.6.1) \]

and

\[ \cos \alpha = \frac{(d/2 - \Delta t/2)/d/2}{1 - \Delta t/d}, \quad (4.6.2) \]

where \( a \) is the arc segment of the roller touched by the tape, \( \alpha \) the corresponding angle, \( d \) the roller diameter and \( \Delta t \) the reduction of the thickness.

The ‘process time’ is the time during which a point of the tape surface is touching the roller:

\[ t_p = \frac{a}{v}, \quad (4.6.3) \]

where \( v \) is the linear roller speed. Hence

\[ t_p = \frac{d}{2v} \cdot \arccos (1 - \Delta t/d). \quad (4.6.4) \]

It follows that \( t_p \) is a function of three process variables \( d, v, \Delta t \). The dependance on \( d \) and \( v \) is obvious; to consider the reduction \( \Delta t \) we make the approximation

\[ \arccos (1 - x) \approx 2 \sqrt{x}, \quad (4.6.5) \]

which is fairly accurate for the small angles involved here, and commonly used in the literature.

If a given reduction \( \Delta t \) is replaced by two rolling passes with reductions \( \Delta t/2 \) each, it follows from equations 4.6.4 and 4.6.5 that

\[ 2 t_p(\Delta t/2) = \sqrt{2} t_p(\Delta t) \quad (4.6.6) \]

i.e. the process time is increased by a factor of \( \sqrt{2} \).

Therefore, by increasing the roller diameter, decreasing the roller speed and decreasing the reduction rate we increase the process time, which in the framework of
the ‘relaxation time concept’ should prevent the formation of ‘sausaging’, in agreement with the experimental results of the previous chapter.

At this stage this model describes only the influence of three operation parameters. To come to a more comprehensive picture, the actual deformation mechanism has to be considered and to be understood. In particular, the influence of the parameters $d$, $v$, $\Delta t$ on the relaxation time has to be made clear. For example, Han and Freltoft [1] point out that a smaller roller diameter results in a ‘higher degree of freedom’ for the powder flow. Translated to the ‘relaxation time concept’, this would mean that the relaxation time with a small roller would be shorter, which must be assessed against the decreased process time. These considerations might hint to an explanation of the contradicting results on the influence of the roller diameter, which was mentioned earlier. On the experimental side, the comparison between different rollers is limited because the friction between roller and tape is an important parameter [10] [11], which is hard to control. Furthermore, the use of a large roller at small thicknesses (below 0.2 mm) is not possible due to the elastic deformation of the roller [10].

A dynamical response to deformation is also known from the classical plastic deformation of metals, known as strain rate effects. It is usually described as

$$\sigma = \sigma_0 (\varepsilon_0 / \varepsilon_t)^m,$$

with $\sigma$ stress, $\varepsilon$ strain [10]. The exponent $m$ strongly depends on the temperature, the material and the work hardening [12]. If

$$m = 1$$

it can be shown that [10]

$$\sigma_0 = 3\eta,$$
where the (Newtonian) viscosity $\eta$ is defined by the relation

$$\tau = \eta \frac{dy}{dt}$$

between the shear stress $\tau$ and the shear strain $\gamma$.

These equations describe a direct connection to fluid dynamics and might be used as the starting point of a quantitative expansion of the 'powder flow model' of Han and Freltoft [1].

### 4.6.7 Other Defects related to the Silver Sheath

#### I Cracks and Intergrowth

During the mechanical deformation, cracks were sometimes observed to form both in the silver sheath and the HTS core. While the latter is a direct interruption of the current path, cracks in the silver sheath were also found to be detrimental to the tape properties. Fig. 4.6.12 shows the interface region of a tape with a small crack in the sheath. Presumably, some precursor powder had been pressed into the crack during mechanical deformation, which led to the growth of a Bi2223 grain perpendicular to the tape direction. (This demonstrates again, that the Bi2223 platelets grow preferably parallel to the interface, see Ch. 4.5.1) The presence of the grain grown perpendicular disturbed the Bi2223 texture, and probably led to a reduction in critical current. It was also observed, that Bi2223 grew into the silver sheath, as shown in Fig. 4.6.13. Whether this intergrowth phenomenon was also originally caused by cracks in the sheath, was unclear.
Fig. 4.6.12: Interface region of a Bi2223 tape, with a crack in the silver sheath, and a Bi2223 grain grown out of the crack

Fig. 4.6.13: Bi2223 multifilament tape with a Bi2223 grain grown into the silver sheath
In some cases, macroscopic cracks formed at the tape edges during mechanical deformation, such that the core was exposed to air. This was found to be very detrimental to tape properties, as during sintering, some liquid phase would ‘leak’ to the outside, and consequently the Bi2223 formation was inhibited. Formation of these large cracks could be prevented by reduction of deformation rate, reducing the initial fill density of the powder and annealing of the tape.

II Contamination

Some silver tubes were found to be contaminated at their inner surface with small silicon (or silica) and aluminium (or alumina) particles. Fig. 4.6.14 shows the inner surface of a silver tube, with a black silicon (or silica) particle. It was first attempted to clean the tubes from these particles with an ultrasonic bath, but unsuccessful. Then a chemical treatment was tested, by submersing the tube for several hours in boiling, concentrated NaOH. After this treatment, the visible Si particles had disappeared; however, a tape made from such a tube had poor microstructure of the superconducting core and zero critical current. The tube was obviously contaminated, either with the Sodium from the NaOH, or from the silicon, now spread over the tube surface, but not detectable with SEM.

It can also be seen from Fig. 4.6.14, that the inner surface of the as-received silver tubes was rather rough and uneven, with many cracks. The roughness of the surface, and possibly also the contamination with Si and Al, could be removed by polishing the tube, but on the other hand, polishing (with a diamond paste) would bury the danger of introducing even more contamination. The tubes used in this thesis work were not polished, but cleaned in an ultrasonic bath with isopropanol, to remove grease and dust.
III Blistering

Blistering of the tapes was sometimes observed after sintering, especially in long tapes (30 cm - 10 m). It is, of course, not a defect of the silver sheath, but the Bi2223 precursor powder (see Chapter 4.2.4). Possible reasons could be trapped gas or moisture in the powder, development of carbon dioxide from residual carbonates, or release of oxygen from Bi2212 or other phases. The size of the blisters ranged from 1 mm to tapes blown up over 10 cm or more. While blisters were observed mainly after the first heat treatment, their detrimental effect on superconducting properties became obvious only after the final, second heat treatment. Careful analysis showed that usually no reduction of the critical current was seen across the blister after the first sintering, but always after the second heat treatment. Systematical heating experiments showed that tape blistering
occurred in the temperature range between 600 and 650 °C, but other researchers found contradicting results [14]. Apparently, there is more than one cause for the blistering phenomenon. Blistering was found to be one of the main obstacles in reaching the same level of critical current in long tapes as in short samples. This problem has to be overcome in order to produce tapes suitable for industrial scale applications.

4.6.8 Summary

A parameter study of mechanical deformation (rolling) showed that the formation of 'sausaging' in rolled HTS/Ag tapes depended on the parameters of the deformation process, but not on the starting conditions of the tape itself. As the overall density of the oxide core increased only in the early stages of the rolling schedule, no direct causal relationship was identified between the density and the interface distortion, which onset in the later rolling stages. Using large silver particles as a 'tracer', a non-uniform, wavy powder flow could be observed even at earlier stages. It was not confined to the sheath-core interface, but can be seen inside the bulk oxide core. Thus the wavy flow seems to be an intrinsic property of the powder transport. A close relation between sausaging, necking and shear bands was identified.

A theoretical model of the mechanical deformation was developed, emphasising the dynamical view by assuming a relaxation time of the powder flow. Calculating the rolling process time yielded some quantitative predictions which agreed with experimental results, but for a comprehensive understanding of the problem the deformation has to be considered explicitly. A 'flow model' is apparently a useful starting point for a quantitative modelling. Experimentally, the described method of monitoring the core powder flow with silver particles could be used for further and systematical investigations.
Some other defects related to the silver sheath were also identified. Cracks in the silver at the interface, contamination of the silver with Si and Al, and blistering during heat treatment were all found to have a negative influence on the final tape properties.

References


[14] M. Ionescu, personal communication


4.7 Two-Step Sintering of Bi2223 Tapes

4.7.1 Introduction: Optimization of heat treatment parameters

The final step of tape processing was the heat treatment of the tape. It was carried out in two thermal cycles, with intermediate deformation in order to improve texture and density. The Bi2223 phase forms only in a narrow temperature window around 840 °C, and therefore the tape heat treatment required very accurate temperature control in the furnace. While the optimum sintering temperature was found to be 840 (±3) °C for practically all precursor powders (Chapter 4.1.3 [Fig. 4.1.7] and 4.4), the optimum sintering time depended on the particular powder being used. The duration of the first sintering cycle was typically 35-50 hours. It was aimed to reach an incomplete phase transformation, from Bi2212 into Bi2223 by 80-90 percent. The Bi2223 grains were then further textured and densified during the intermediate deformation, while the residual unreacted powder (Bi2212 and secondary phases), was required in the second sintering cycle, to heal the damage caused by the intermediate deformation. The second sintering cycle was carried out in a two-step process, with 20 - 40 hours at 840 °C, and then 25 - 50 h at 810-820 °C. The optimum duration again varied between different precursor powders, while the optimum temperature of the second step will be discussed in Chapter 4.7.4. This two-step process was found to result in strongly increased critical currents compared to one step only, and the rest of this chapter will focus on investigating the microstructural origin of this improvement.

It has also been reported by several research groups that critical current densities can be improved if the tapes are slow-cooled at the end of the final sintering stage [1,2,12]. An improvement in both the grain connectivity [2,12] and flux pinning [3,12] has been proposed to explain the improvement in J_c during cooling. Here it will be
demonstrated that improvement through slow cooling and two step sintering rely on the same effect.

Other groups have reported that even the heating rate of the tape sintering has a strong effect on the final tape properties, and that no Bi2223 forms at all, if the tape is heated very fast [10]. Very fast cooling also has a detrimental effect, probably due to crack formation caused by thermal stress. The heat treatments carried out in this thesis work usually were carried out with heating and cooling rates of 3 - 4 °C/min.

4.7.2 Experimental Details

In order to investigate the effects of two-step sintering and slow cooling, a series of short samples (4 cm) were initially sintered at 840 °C in air, cooled, then rolled to 200 μm thickness, and then further sintered. For the second sintering stage, four different schedules were used, summarized in Fig. 4.7.1. The first group of tapes was treated for 50 h at 840 °C, then furnace cooled at around 4 °C/min (denoted as ‘1step’). The second group (‘2step’) was subjected to an additional annealing step at 820 °C for 50h and then furnace cooled. A third batch was sintered at 840 °C for 50h, slow cooled at 0.8 °C/h to 800 °C, and then furnace cooled (‘1step+SloCo’). The second and third schedule had approximately the same total sintering time. The fourth heat treatment (‘2step+SloCo’) was a combination of two step and 1step+SloCo, i.e. after 50 h at 840 °C the tapes were slow cooled to 820 °C, held for 50 h, then further slow cooled to 800 °C. Critical currents (Ic) of the tapes were measured using a criterion of 1 μV/cm with an applied magnetic field perpendicular to the tape plane surface. AC susceptibility measurements were carried out to investigate superconducting properties at lower temperatures. The phase composition and microstructure of peeled tape samples and polished and etched cross sections of tapes were examined using XRD and SEM.
CHAPTER 4.7: TWO-STEP SINTERING OF Bi2223 TAPES

Fig. 4.7.1: Heat treatment schedules for 4 groups of tapes
4.7.3 Effects of two step sintering and slow cooling

a) Superconducting properties

Fig. 4.7.2 shows results of $I_c(B, 77K)$ measurements on the tapes subjected to the four different heat treatments. The superconducting properties of the ‘1step’ tape were much inferior when compared to those of tapes made using both the ‘2step’ and slow cooling methods. Zero field $I_c$ for the 1step tapes is only 50% of the 2step tapes, which is attributable to the additional annealing step at 820 °C in the latter case. Most remarkable, however, is the fact that both the 2-step and slow cooling methods result in critical currents $I_c(B)$ falling on one curve ($I_c(0 T) \approx 10^4$ A/cm²). Furthermore, the combination of ‘2step’ and slow cooling does not further increase the critical current. This strongly indicates that (a) the $I_c$ increase after slow cooling and 2step sintering originates from the same microstructural effect, and (b) there is a saturation of this effect. (Results from a variation of the duration of the second step, not shown here, show a similar saturation.)

A first clue to the nature of this effect can be found in a normalized display of $I_c(B)/ I_c(0)$ of the critical currents, as shown in the inset of Fig. 4.7.2. The normalized $I_c$ of the ‘1step’ tapes was more sensitive to small applied fields, but for $B > 20$ mT it was similar to those of the 2step tapes. This indicates that the $I_c(B)$ improvement was mainly caused by an improvement in the grain connectivity.

AC susceptibility $\chi(T)$ of tapes was measured at various magnetic fields, after the first sintering and after the second sintering with one-step and two-step processes, respectively. The $\chi(T)$ data in zero external field are shown in Fig. 4.7.3, showing that the critical temperature (here defined as the peak in Im $\chi$) increased from 100 K after the first sintering, to 102 K after one-step sintering, and further to 104 K after two-step sintering. The sample shows a double-step transition after the first heat treatment, which
disappears after the second treatment. The origin of this double step is unknown, but it was confirmed with several samples. The results of measurements in magnetic fields were summarized in Fig. 4.7.4, which displays the peak temperatures of $\text{Im} \chi(T,B)$. It was found that the peak temperature was higher at all fields of the tape processed with two-step sintering, compared to the one-step samples. This indicates that also at lower temperatures and in higher magnetic fields, two-step sintering results in superior superconducting properties.

![Graph showing critical currents of tapes with four heat treatments.](image)

**Fig. 4.7.2:** Critical currents of tapes with four heat treatments; at 77K against magnetic field perpendicular to the tape.
Fig. 4.7.3: Magnetic susceptibility $\chi(T)$ of tapes after the first heat treatment, and after second heat treatment with one-step and two-step sintering, in zero magnetic field
Fig. 4.7.4: Peak Temperature of Im(χ) against magnetic field; for tapes after the first heat treatment, and after second heat treatment with one-step and two-step sintering

b) Microstructure

Fig. 4.7.5 shows the XRD patterns of four tapes sintered in the four schedules described earlier. While in all cases Bi2223 peaks are dominant, two differences exist between the ‘1step’ sample and the 2step tapes: Bi2201 (hkl) peaks are only visible in the ‘1step’ sample. These peaks were not detected in the two stage tapes, but a higher (hkl) intensity of Bi2212 was found in the 2step and ‘SloCo’ tapes. SEM micrographs shown in Figs. 4.7.6 a,b,c show this difference more clearly. Bi2201 (white, confirmed by EDS) is evident in the tapes after the first sintering (Fig. 4.7.6 a) and after a ‘One Step’ second sintering (Fig. 4.7.6 b). In the tapes subjected to either the ‘2step’ sintering (Fig. 4.7.6 c) or slow cooling, Bi2201 was not found, but Bi2212 (and other secondary phases) were present.
Fig. 4.7.5: XRD scans of tapes after the second heat treatment; sintered with four heat treatments described earlier
Fig. 4.7.6 a,b: SEM micrographs of tapes a) after the first heat treatment, b) after second heat treatment with one-step sintering
c) Discussion

The results presented above leave open two possible mechanisms that could cause an increase in the critical current:

1. The removal of the Bi2201 from grain boundaries increases the number of 'strong links' in the tape;
2. Additional pinning centres are created through decomposition of Bi2223 into Bi2212 and other secondary phases.

To decide which of these explanations is more favourable, we return to the analysis of our $I_c(B)$ curves in Fig. 4.7.2. The normalized data in the inset indicate a 'grain boundary weak link effect' because the difference in $I_c - B$ performance for the different tapes is only limited to the low field region. An even stronger indication for this cause is the apparent saturation of the $I_c$ improvement. The saturation can be well
explained by the removal of Bi2201 from grain boundaries. Once Bi2201 is completely removed, I\(_c\) would not further increase from prolonged annealing and slow cooling, as shown in the fourth sintering schedule. There was no indication of improvement in flux pinning, since at slightly higher fields all four normalized I\(_c\) -B curves overlap. Furthermore, it seems that the secondary phases created during the decomposition are physically too large to act as effective pinning centres. The possibility of improved flux pinning from secondary phases has been investigated in more detail by Wang et al. [4] and Horvat et al. [5], who arrive at the same conclusion via analysis of magnetic measurements. In contrast, Parrell et al. [12] found that that the tapes subjected to slow cooling also show higher critical currents in higher magnetic fields. While they confirm the presence of Bi2201 and its removal during slow cooling, they also show strong evidence that the flux pinning is improved through slow cooling. They argue that this may be caused not (only) by secondary phases, but through improved intrinsic pinning; caused by changes in oxygen content or cation stoichiometry in the Bi2223 grains. Such a change of intrinsic pinning properties would also be consistent with the saturation of J\(_c\) improvement (as function of sintering time) shown in the previous chapter. In the light of these considerations, a final judgement on whether the removal of Bi2201 from grain boundaries is the only cause for improved critical currents after two-step sintering or slow-cooling can not be made.

The strongly negative effect of Bi2201 is attributed to a combination of the following factors. Bi2201 is non-superconducting at all temperatures measured, and in contrast to other impurity phases which have an irregular or spherical shape, Bi2201 has an elongated, plate-like morphology. These non-superconducting Bi22201 layers, residing along Bi2223 colony boundaries, form powerful blockages to the current flow between the Bi2223 colonies which form a percolative network within the tape.
Furthermore, the presence of Bi2201 implies that there must also be other impurity phases coexisting in the, since the overall composition is fixed.

When comparing the results shown here with those of other groups, it is important to consider the temperature range of the slow cooling/annealing. This point was investigated by Liu et al. [6]. In this thesis, no results are shown from slow-cooling or annealing the tapes below 800 °C, as this has been shown in Chapter 4.2.2 to lead to formation of ‘3221’, which appears to be detrimental to the superconducting properties [6][8].

But even at 820 °C, Bi2201 is most likely to decompose via the reaction [9]

\[ \text{Bi2201} + \text{Bi2223} \leftrightarrow 2 \text{Bi2212}, \]  

i. e. decomposition of Bi2223. Additionally, Bi2223 may decompose into other, non-superconducting phases. To avoid these detrimental side effects, the question arises how to avoid the formation of Bi2201 from the start, or, alternatively, whether the resultant Bi2212 can be further converted to Bi2223 without the reappearence of Bi2201. An attempt was made, by subjecting a tape to a two-step sinter, and then to a third heat treatment at 840 °C. After the third heat treatment, the critical current dropped from 31 A to 12 A, which was almost the same value obtained if the second sinter consisted of one step only. In an XRD measurement, shown in Fig. 4.7.7, it was found that Bi2212 disappeared, while the Bi2201 phase had reappeared after the third heat treatment at 840 °C. It can be concluded that reaction (1) is reversible, and with it the critical current.
Fig. 4.7.7: XRD scans of tapes after the second, two-step sintering stage, and after a third heat treatment at 840 °C for 30 h
4.7.4 Optimization of the ‘decomposition step’ temperature

Another conclusive proof of the strong correlation between presence of Bi2201 and the critical current was found by optimizing the temperature ($T_{22}$) of the ‘decomposition’ step for different tapes. Fig. 4.7.8 shows the final critical currents as function of the decomposition step temperature, of tapes made from three different powders. Powder A was a commercial powder purchased from Merck (UK) Ltd. (labelled and described as ‘Powder B’ in Chapter 4.4). After filling the powder into the silver tube, powder A was subjected to an additional heat treatment at 830 °C for 5 h (‘high temperature degassing’ [11]). Powders B and C were ‘home-made’. Their stoichiometry and processing parameters were described in chapter 4.1, where they were labelled as P3 and P4, respectively. The tape made from powder A was a multifilamentary tape with 27 filaments, while tapes made from powders B and C were monofilamentary tapes.

Fig. 4.7.8 shows that the optimum decomposition step temperature ($T_{22}$) for tapes B and C, made from powders B and C, was 815 °C. In contrast, in tape A the highest critical current was found at $T_{22} = 825$ °C. SEM investigations revealed, that this difference was linked to the presence of Bi2201 in the tapes. Fig.s 4.7.9 and 4.7.10 show SEM micrographs of tapes A and B after the second heat treatment, with $T_{22} = 815$ °C and 825 °C, respectively. While in both cases no Bi2201 was found if $T_{22}$ was 815 °C (Fig.4.7.9 a and b), after sintering with $T_{22} = 825$ °C, Bi2201 was present in tape B, but not in tape A, as shown in Fig. 4.7.10. Tape C, not shown here, also contained residual Bi2201 after sintering with $T_{22} = 825$ °C. The presence of Bi2201 in tapes B and C resulted in lower critical currents at $T_{22} = 825$ °C, while in tape A the critical current was highest at this temperature.
The different phase assemblage at 825 °C, i.e. presence or absence of Bi2201, could be caused by different stoichiometry, or powder processing. While the reason for the different behaviour of the powders is not understood, their comparison clearly demonstrates the importance of Bi2201 phase for the tape properties.

Fig. 4.7.8: Critical current of tapes A, B, C as function of the 'decomposition step' temperature $T_{22}$
Fig. 4.7.9: SEM micrographs of tapes A and B, sintered with $T_{22} = 815 \, ^{\circ}C$
Fig. 4.7.10: SEM micrographs of tapes A and B, sintered with $T_{22} = 825$ °C
4.7.5 Summary

It was shown that a two step sintering process can strongly improve critical current density in Bi2223 tapes, attributable to the removal of Bi2201 in the annealing step at 820°C in a two step sintering cycle. A comparison with, and combination of slow cooling reveals that both methods essentially have the same effect. The detrimental effect of Bi2201 in $J_c$ is attributed to a combination of its non-superconducting nature, plate-like morphology and distribution along Bi2223 colony boundaries, forming powerful blockages to the current flow between Bi2223 colonies. Optimization of the temperature of the second step in different tapes further confirmed the importance of the Bi2201 phase.

References


4.8 Fundamental Aspects of Bi2223 Phase Formation and Stability

The previous chapters 4.1 to 4.7 focussed on processing parameters and their influence on microstructure and superconducting properties of Bi2223 tapes. This chapter, in contrast, takes a look at Bi2223 formation from a fundamental point of view. Some basic models of Bi2223 formation, which have been proposed in the literature, will be reviewed and compared. A new mechanism will be proposed. A number of relevant experimental results, some from this thesis work and some from the literature, will be summarized.

4.8.1 Bi2223 Formation Rate and Avrami Equation

A number of authors [1-7] have investigated the Bi2223 formation by measuring XRD scans after various tape sintering times, and comparing the experimentally found formation rate to those predicted by various models. This was done by fitting the time dependence of the formation rate to an Avrami equation [25-27]

\[ V = 1 - \exp (-C t^n) \]

where \( V \) is the Bi2223 volume fraction, \( t \) is the time and \( n \) an exponent characteristic for each formation model. \( C \) is the formation rate constant, assumed to be given by an Arrhenius law

\[ C = C_0 \exp \left( \frac{E_{\text{act}}}{k_B T} \right) \]

with \( E_{\text{act}} \) the activation energy, \( T \) the temperature, and \( k_B \) the Boltzmann constant.

While most authors found that it was best described with an Avrami equation of a diffusion-controlled, two-dimensional nucleated growth, the numbers found for \( n \) and
$E_{\text{act}}$ varied considerably. Luo et al. [2] showed that only one of their precursor powders used followed this dependence, while in the other one, the formation started only after a delay period, and could not be described by the Avrami equation. A similar delay period was also found in the in-situ XRD measurements by Thurston et al. [8], and in some of the powders in this thesis work (Chapter 4.3.3, Fig. 4.3.5 and Chapter 4.4.4, Fig. 4.4.3).

This delay effect was discussed in Chapter 4.3, and explained with the 2-stage formation model of Jeremie et al. [4], which states that Bi2223 forms from Bi2212 only after the incorporation of lead into the Bi2212 phase:

$$\text{Bi2212} + \text{SP} \rightarrow (\text{Bi,Pb})\text{2212} + \text{SP} \rightarrow \text{Bi2223} \quad (1)$$

Some evidence for this model was presented in Chapter 4.3. It can be reconciled with the Avrami model, by assuming that only the second part of the two-stage reaction is described by the Avrami equation. However, this hypothesis was not tested quantitatively.

Grivel et al. [5] found that the activation energy $E_{\text{act}}$ is very sensitive to the processing parameters heating rate, sintering time and temperature, powder particle size and composition. They therefore labelled $E_{\text{act}}$ the 'apparent activation energy', because it is not a constant. Consequently, the time and temperature dependence of the formation rate $V$ is implicitly much more complex than it appears from the Avrami equation.

Furthermore, considering the platelike shape of the Bi2223 grains, and the polycrystalline morphology, it is not surprising that a 'two-dimensional nucleated growth' model was found to fit the XRD data. In summary, the Avrami equation can be successfully applied to describe Bi2223 formation rate by assuming a two-dimensional, nucleated, diffusion controlled growth, but it does not really increase our understanding of the complex formation process.
4.8.2 Role of Liquid Phase and Bi2212 in Various Models

There are also many contradicting reports on whether the Bi2223 phase grows from a liquid phase or directly from the Bi2212 phase. This is essential for the question whether the Bi2212 texture, created through both mechanical deformation (Chapter 4.2.2) and recrystallization (Chapter 4.3), is transferred to the Bi2223 morphology.

A number of growth models have been proposed, and for each evidence has been produced from microstructural investigations. An extensive review was given by Wu et al. [28]

Growth from liquid

It has been proposed [9,10] that Bi2223 grows not directly from the Bi2212 phase, but from a (partial) liquid phase. This means that in the reaction equation (1) an additional step has to be added:

\[ \text{Bi2212 + SP} \rightarrow (\text{Bi,Pb})2212 + \text{SP} \rightarrow \text{Liquid} \rightarrow \text{Bi2223} \]  

The growth from liquid was observed directly by Morgan [9], who found droplets on the surface of growing grains. Grivel and Flükiger [10] observed growth from liquid in pellets, by sintering them for various times and examining the same spot after each sintering. Lanagan et al. [11] have measured liquid formation with an in-situ ultrasonic technique.

The work carried out for this thesis found evidence for liquid phase formation mainly in the vicinity of the silver sheath. DTA measurements of precursor powders showed that, except in very poor powders, the melting onset temperature was always above the tape sintering temperature (e.g. Fig. 4.1.3). It was stated in Chapter 4.2.2 that if a powder had a melting onset below the tape sintering temperature, the abundance of liquid always resulted in very poor tape microstructure (Fig. 4.2.8.)
On the other hand, the evidence in the literature ([9-11,28] and Ref.s therein) suggests that there is some liquid phase present during sintering even in high quality tapes. In SEM investigation during this thesis, some evidence was found for a liquid phase. This is shown in Fig. 4.8.1. The SEM micrograph shows a high angle grain boundary, with some residual phase trapped between the grains. While the composition of this phase could not be identified, it appears to have been in a liquid state, and to have been in intimate contact with the Bi2223 grain on the right. Whether this Bi2223 grain has actually grown from the liquid (?) phase, is not clearly visible.

Fig. 4.8.1: SEM backscattering image of a high angle grain boundary in a Bi2223 tape; after the first sintering stage

It was pointed out in Chapter 4.5.1, that close to the silver interface, phase relations are very different compared to the bulk. In a DTA measurement of a mixture of Bi2223 precursor and silver powders, the melting onset was as low as 810 °C, indicating that there would be liquid phase present during tape sintering at the silver sheath.
Glowacki et al. [14] have shown in an elegant experiment, how the silver surface promotes the Bi2223 growth by surface diffusion. At the interface, in contrast to the bulk, the liquid phase formation is beneficial, because by wetting of the silver interface the Bi2223 phase grows highly aligned.

It was also found that in multifilamentary tapes, Bi2223 forms faster compared to single filament tapes [12,13,17]. This can be explained as a consequence of the strongly increased interface area in multifilamentary tapes, in combination with the fact that the formation speed of Bi2223 from a liquid phase is probably much faster compared to a solid state growth. The difference in formation speed between mono- and multifilamentary tapes can also be interpreted as an argument against the theory of growth from liquid phase in the bulk tape, because if the Bi2223 phase would grow from liquid both in the bulk and at the silver interface, there would be no difference in formation rate. Wu et al. [28] arrive at the same conclusion through extensive investigations of quenched tapes with TEM and in-situ XRD. Another important argument against the growth-from-liquid model is the strong correlation between the Bi2212 and Bi2223 texture, which was shown by transmission XRD experiments [15-19,28], and the dependence of the Bi2223 grain size on Bi2212 recrystallization, which was demonstrated in Chapter 4.3.

**Intercalation**

A model that would be in favour of a strong correlation between Bi2212 and Bi2223 morphologies, is the growth of Bi2223 by intercalation of CaO and CuO layers into the Bi2212 lattice. Evidence for such a mechanism was shown in TEM investigations by Wang et al. [16] and Luo et al. [2]. Both groups show that the transformation is assisted by the presence of a liquid phase. However, in contrast to the liquid phase growth model described in the previous section, here the liquid is only
locally present at the grain boundaries. The Bi2212 morphology is conserved by a direct transformation from Bi2212 into Bi2223 crystals.

**Epitaxial growth**

During microstructural work for this thesis, evidence was found for a third mechanism, epitaxial growth of Bi2223 on Bi2212 templates. This is shown in Fig. 4.8.2 and 4.8.3. The Bi2223 phase has grown from a reaction between the Bi2212 and Sr$_x$Ca$_y$Cu$_z$O$_d$ phases. This mechanism also conserves Bi2212 texture and morphology, in particular the correlation of Bi2212 and Bi2223 grain size, which was discussed in Chapter 4.3. Epitaxial growth model does not explain, however, how the Bi2212 template itself is transformed into Bi2223. It must also be said, that this type of growth was observed only rarely.

**Fig. 4.8.2: Bi2223 growth on the sides of a Bi2212 ‘template’**
Fig. 4.8.3: a) Epitaxial growth of Bi2223 phase on both sides of a Bi2212 crystal; in a Bi2223 tape after 50 h sintering (SE mode)
b) the same area in a backscattering image: dark grey: Bi2223; light grey: Bi2212; black: cuprate
Solid State Intergrowth

By far the most frequent growth ‘mode’ observed in SEM investigations was Bi2223 grains growing through Bi2212 grains with an angle between them, as shown in Fig. 4.8.4 and 4.8.5. A liquid phase, could not be found to be involved in this growth mechanism, but might be locally present on a scale not accessible with SEM. It is proposed to label this type of growth “solid state intergrowth”. Intercalation growth can be regarded as a special case of this mechanism, with zero angle between the grains.

Low angles between the ‘parent’ (Bi2212) and ‘daughter’ (Bi2223) grains are probably favourable in terms of growth speed, because the dissolution of the Bi2212 along a-b planes simultaneously provides all the atomic components of the ‘daughter’ grain. Growth with low angle is also more likely to produce large grains, because a Bi2223 grain growing with a high angle through the Bi2212 parent grain would probably grow only very slowly, once it reaches the grain boundary. Short grains are possibly later dissolved by Ostwald ripening or overgrown by recrystallization.

Assuming this hypothetical scenario, the ‘solid state intergrowth’ mechanism can explain the fact that Bi2223 texture and grain size in the final tape strongly depends on Bi2212 morphology and recrystallization, as was shown in Chapter 4.3.
Fig. 4.8.4: SEM micrograph of a tape after the first sintering stage; Bi2223 phase (dark grey needles) growing through a Bi2212 crystal (light grey)

Fig. 4.8.5: A Bi2223 tape after 10 hours of sintering; Bi2223 phase (dark grey) growing through Bi2212 crystals (light grey)
Direct decomposition of Bi2212

Finally, decomposition of Bi2212 without involvement of secondary phases has also been considered in the literature [19]:

\[2 \text{Bi2212} \rightarrow \text{Bi2223} + \text{Bi2201}\]

While this is certainly not a major reaction channel in tapes, the presence of small amounts of Bi2201 at the end of the first sintering stage (see, for example, Fig. 4.3.4, p. 94, Tape A and Fig. 4.7.5, p. 156) indicates that this Bi2201 is the result of such a decomposition. It was also observed during this thesis work (Fig. 4.3.4), that the Bi2201 phase appears only towards the end of the sintering. In the final stage of sintering, when the transformation from Bi2212 to Bi2223 is almost complete, a direct decomposition from Bi2212 \(\rightarrow\) Bi2223 + Bi2201 probably occurs locally, because there are no secondary phases 'available' for transforming Bi2212.

In summary, it can be assumed that all these formation mechanisms are possible, and are in fact competing in tape sintering. The fact that the Bi2212 and Bi2223 textures are closely linked indicates that direct growth from Bi2212, in intergrowth, intercalation or epitaxial mode, is predominant in the bulk of the tape, while close to the silver interface, growth from liquid phase is the predominant process, as is probably in multifilamentary tapes with many, small filaments. Towards the end of the sintering, some Bi2212 decomposes directly into Bi2223 and Bi2201.

4.8.3 Thermodynamic Stability

The mechanism of the Bi2223 phase formation is closely linked to its thermodynamic stability. It was confirmed during this thesis work, that Bi2223 phase can be formed only in a small temperature window (Chapter 4.1.3), and is very sensitive to
changes in stoichiometry (Chapter 4.1), impurities (Chapter 4.2) and oxygen atmosphere (Chapter 4.3). It was shown in Chapter 4.7 that Bi2223, when slow-cooled from the sintering temperature or annealed slightly below, decomposes. Bi2223, like all HTS, is thermodynamically unstable at room temperature, and belongs to the family of entropy-stabilized compounds [20]. The necessary entropy is supplied by crystal defects. Hence the phase is only stable with non-ideal stoichiometry (Fig. 4.1.1). The dependence of the stability region on oxygen pressure [21] indicates that oxygen disorder also plays an important role. In Chapter 4.3 it was demonstrated that the oxygen pressure in turn is closely linked to the lead distribution, and in particular the solubility of lead in the Bi2212 and Bi2223 phases [22]. As lead is also known to stabilize the Bi2223 phase [23], there is a close link between these two stabilizing factors.

The correlation between Bi2212 stability and its lead content, which was discussed in Chapter 4.3.1, is also a complex one. It was reported [28-30] that during heating of the Bi2223 tapes from room temperature to the sintering temperature, lead first segregates from the Bi2212 phase, but later moves back into the Bi2212. Frello et al. [17] have observed that in their tapes no Bi2223 forms at all if the tape is heated very fast to the sintering temperature, and instead the Bi2212 completely decomposes. Other researchers could not find such an instability [6,24]. This interesting effect may also be linked to the lead and/or oxygen distribution in the specific powder, and is an important benchmark to test theories of Bi2223 formation and stability.

4.8.4 Summary

Various models to describe Bi2223 formation were reviewed. Experimental data on the growth rate can be successfully described with the Avrami equation, assuming a nucleated, two-dimensional, diffusion-controlled growth. However, the Avrami
exponents and activation energies found varied considerably, and furthermore the latter was found to be time and temperature dependence. This implies that the Avrami model is only a first approximation.

Various Bi2223 growth mechanisms were discussed, including growth from a liquid phase, direct growth from Bi2212 by intercalation and decomposition of Bi2212 into Bi2223 and Bi2201. Two new mechanisms were shown to exist in tapes too: Epitaxial growth on Bi2212 templates, and ‘solid state intergrowth’. The latter was proposed to be the predominant mechanism in the bulk of the core, while at the core-silver interface, Bi2223 probably grows from a liquid phase which wets the silver surface.

It was also pointed out that there is a close link between the formation mechanism and the thermodynamic stability, or rather instability, of the Bi2223 phase. A comprehensive understanding of both is essential for further optimization of microstructural and superconducting properties in Bi2223 tapes.

References


[24] U. Balachandran, personal communication


5. Design and Test Results of Current Leads

5.1 200 A Leads for SMES Research at Monash University

5.1.1 SMES Requirements and Current Lead Design

The Centre for Power Engineering (CEPE) at Monash University, Melbourne, conducts research on a small scale Superconducting Magnetic Energy Storage (SMES) system. The work focuses on stability enhancement in power systems, where the SMES magnet is used to balance load fluctuations [1,2].

In 1995 the CEPE designed a new superconducting NbTi coil. It was aimed to produce a magnetic field of 7.6 Tesla (equivalent to 26 kJ electrical energy) at a maximum current of 110 A. To reduce the helium consumption, it was decided to operate the SMES with a HTS current lead, which had to be built at Wollongong University, as part of this thesis. The specifications for the current lead were determined by the current capacity of the NbTi coil and the dimensions of the SMES helium dewar. Fig. 5.1.1 shows a photograph of the SMES system, and Fig. 5.1.2 a drawing with the dimensions of the helium dewar for the SMES magnet. The two main requirements were

1) current capacity above 110 A (in a magnetic stray field of the coil)
2) total length around 1 m
3) deliberate load fluctuations, i.e. possible overcurrents and coil quench
4) frequent cooling cycles (as the insulation properties of the dewar were insufficient to allow permanent He cooling)

As a consequence, the current lead had to be constructed in a way to sustain possible overloads without burnout, and frequent thermal cycling without degradation. It was already pointed out in Chapter 2 that, regarding these two aspects, current leads
utilizing HTS tapes are superior to those with bulk HTS conductors. The silver sheath supplies both an emergency current path, and mechanical and chemical protection of the HTS core.

Fig. 5.1.3 shows a schematic drawing, and Fig. 5.1.4 photographs of the current leads that were designed and constructed according to these requirements. The tapes are encapsulated in a steel cover, and held by screwed plastic clamps. The steel frame provides mechanical protection as well as a guide for helium vapour. The leads were therefore vapour cooled along their entire length. Clamps were positioned every 5 cm, ensuring sufficient mechanical support against Lorenz forces. While the lower part (65 cm) of the lead contains HTS tapes as conductor, the high temperature part (35 cm; 70 - 300 K) is equipped with copper braid. The HTS tapes and copper braid were connected with soft solder. The terminals at both ends were made of copper rings, ensuring sufficiently low contact resistance. In the SMES dewar, the current leads were held with brass clamps on the terminals. Both the HTS tapes and copper braid were soldered to the inner face of the ring terminals. While the ring at the low temperature end was fixed directly on the steel frame, the upper end ring was connected via a steel spring, allowing for thermal contraction of the lead while fixed on a rigid frame. A major advantage of the round copper terminals is, that the leads can be rotated such that the tape face is parallel to the magnetic field of the coil, thus minimizing the reduction of critical current by the magnetic field.

Using screwed clamps for the HTS tapes allows addition, exchange or removal of individual tapes (or copper braid). The current capacity can be adjusted to demand by changing tapes. For the application in the CEPE SMES, three HTS tapes were mounted on each lead. The critical current of each tape was around 30 A at 77 K in self field. The sheath material was high purity silver.
Fig. 5.1.1: Photograph of the SMES setup at Monash University; The Helium dewar containing the superconducting coil is at the centre, the Helium recovery pump on its left, and power supply and control electronics on the right.
Fig. 5.1.2: Drawing of the He dewar for the SMES magnet
Fig. 5.1.3 Schematic drawing of current lead
Fig. 5.1.4a: Current leads, one with steel cover detached (right) and one assembled (left)
Fig. 5.1.4b: High Temperature End of the Current lead
Fig. 5.1.4c: Low temperature end of the Current lead
5.1.2 Test Results

A first, and important step in determining the properties of the current lead is to consider the characteristics of individual tapes. Fig. 5.1.5 displays a Current - Voltage characteristics of a tape similar to those which were used in the current leads. While the critical current derived from 1 μV/cm was found to be 50 A, the current could be increased up to 100 A without quenching the superconducting state.

The second tape property crucial for current leads is the temperature dependence of the critical current $I_c(T)$. Fig. 5.1.6 shows a measurement which was carried out at the University of Zagreb in Croatia. The strong $I_c(T)$ dependence implies that the temperature at the upper end of the HTS part will be crucial for the overall critical current. This point is further evaluated in the theoretical treatment in Chapter 5.3.

The length of the tapes that was chosen for the leads was 65 cm. From a rough estimate, this should ensure that the temperature at the joint is around 60-70 K, and thus the critical current would be well above the critical current at 77 K.

As the first test of the current lead itself, its Current-Voltage characteristics was measured at 77K, i.e. submersed in liquid Nitrogen, as shown in Fig. 5.1.7. 4 voltage taps were attached to measure voltage drops along the various parts of the leads. The total voltage along the entire lead was 14 mV, the largest part of it from the copper part. All connecting parts showed very low voltage, below 2 mV at 100 A. The voltage along the HTS tapes was zero up to around 80 A.
Fig. 5.1.5: Current-voltage characteristics at 77 K of a 40 cm long tape. The voltage was stable and reproducible up to 100 A.

Fig. 5.1.6: Critical current as function of temperature of a tape in self field.
After the successful test at 77 K, the leads were transported to Monash University for implementation into the SMES system. The leads were attached to the frame, which also holds the NbTi magnet, with brass clamps around the copper terminal rings. They also serve as electrical connections.

The leads were tested in the Helium dewar, which was shown in Fig. 5.1.1 and Fig. 5.1.2. The liquid helium level was a few cm above the lower end of the leads. The first test was carried out with a short circuit between the leads, i.e. with the magnet disconnected. The test result is shown in Fig. 5.1.9. Within the resolution of the voltmeter (1 mV), no voltage was measured along the HTS tapes. The voltage at 200 A along the entire lead was 85 mV in one case, and 70 mV for the second lead.

The second part of the test was carried out with the NbTi magnet connected, shown in Fig. 5.1.10. The magnetic field was measured at the lower end of one of the
leads, shown in Fig. 5.1.11 as a function of the current. At 200 A, the tangential stray field at the lower end of the leads is 400 mT. However, no voltage was detected along the HTS part of the lead, with currents up to 200 A. Hence the magnetic field had no effect on the performance of the lead up to 200 A. This could be expected, as the leads were mounted such that the HTS tape plane was parallel to the field of the coil.

The temperature profile along the lead was also measured. It was found that the temperature at the upper end of the HTS tapes was 50 K, i.e. much lower than 'planned' in the design. As the overall critical current of the lead will be determined by the critical current at this temperature, one can, from the data and fit function shown in Fig. 5.1.6, estimate the critical current of the lead to be around 300 A.

The heat leak at zero current was determined to be around 1 litre/hour. For optimized copper leads rated for 300 A, one would expect (see Chapter 2.1)

\[(\Delta V/\Delta t)_{\text{opt}} \approx 0.3 \text{ litres/hour} \quad (\text{at 0A})\]

Therefore, while the electrical properties of the leads were fully satisfying, the heat leak was found to be much too high. The heat leak can be reduced by using tapes with an alloyed silver sheath, and by tapering the lead. The second method relies on the strong temperature dependence of critical current density, which was shown in Fig. 5.1.6. From these data and thermal conductivity data of silver, which are shown in the inset of Fig. 5.1.12, the critical current of one tape was calculated as function of position in a gradient \(4 \text{ K} < T < 77 \text{K}\), as shown in Fig. 5.1.12. From Fig. 5.1.12 it is clear that, along most of its length, the lead is oversized in terms of critical current. By using more tapes at the high temperature end, the heat leak can be reduced without decreasing the overall critical current. This possibility is utilized in the second 'generation' current lead, which will be described in the next chapter. A theoretical treatment of tapered current leads will be given in chapter 5.3.
Fig. 5.1.8: NbTi Coil and HTS Current leads mounted
Fig. 5.1.9: Current Voltage characteristics of the current leads without magnet
Fig. 5.1.10: Current Voltage characteristics of the current leads with magnet connected (kinks in the voltage curves result from refilling helium)
CHAPTER 5.1: CURRENT LEADS FOR SMES AT MONASH UNI

Fig. 5.1.11: Radial magnetic field (from NbTi magnet) at lower end of leads

Fig. 5.1.12: Critical current vs. position $I_c(x)$ of a tape in a temperature gradient $4K < T < 77K$, calculated from data $I_c(T)$ and fit in fig 5.1.6 and thermal conductivity data $k(T)$ shown in the inset (from Ref. [3])
5.1.3 Summary

A pair of current lead was designed for a Superconducting Magnetic Energy Storage (SMES) Research facility at Monash University. The conducting elements were Bi2223 tapes for the low temperature part (65 cm), and Copper braid (35 cm) for the high temperature end. The leads were designed to allow (i) vapour cooling and (ii) exchange or addition of tapes. This was achieved by clamping the Bi2222 tapes and the braid with screwed clamps and encapsulating them into a steel frame. Copper ring terminals allow rotation of the leads, in order to minimize the influence of the magnetic stray field of the SMES coil. The electrical performance of the leads was fully satisfying, as no voltage was detected along the HTS tapes, with currents up to 200 A and stray magnetic fields up to 400 mT. However, the heat leak was high, because Bi2223 tapes with high purity silver sheath were used. In the future, these should be replaced with alloy sheath tapes.

References


5.2 2kA Current Leads

5.2.1 Design

For the second generation of current leads, a current capacity of 1 - 2 kA was envisaged. The design was based on the following characteristics:

- vapour cooling of HTS tapes
- tapering of the leads by using more tapes at the high temperature end (taking into account the strong $J_c(T)$ dependence)
- maximum flexibility of current capacity (and optimum heat leak per current $Q/I$) by allowing exchange of individual tapes

Fig. 5.2.1 shows a schematic drawing, and Fig. 5.2.2 photographs of the lead. The HTS and metal parts were designed as two separate units. The HTS lead is 70 cm long, and has a diameter of 45 mm. A steel rod is at the core of the lead, with steel disks along its length. The tapes are attached to the disks with steel clamps. The entire construction is enclosed (but not sealed) in a steel tube.

The clamps at the ends of the tapes were made of copper instead of steel. They served as electrical connection, and the tapes were soldered onto them. This resulted in a very low contact resistance. The clamps were connected to the end caps of the lead with copper braid. The end caps of the lead were also made of copper. With four threads at each cap, they were screwed onto the other components of the cryogenic system.

The screwed clamp design ensured maximum flexibility; the lead may be optimized (in terms of current capacity) for any given configuration by the addition, removal or exchange of individual tapes. For the test described in the next chapter, 8 groups of tapes were used, each consisting of three tapes, as shown in Fig. 5.2.2a. One tape from each group reached the entire length of 56 cm, the second was 13 cm and the
third 6 cm in length. The optimization of tapered leads is discussed in chapter 5.3, where a formula is derived for the optimum length of the shorter tapes. The tapes were made with a pure silver sheath and had a critical current of 25 A. Pure silver sheath is of course not the most efficient in regard to heat leakage, but nevertheless useful for preliminary tests of the design.

Several voltage taps were soldered to the tapes and other parts of the lead, as shown in Fig. 5.2.2b. The metallic part of the lead (77 - 300 K) is shown in Fig. 5.2.2 c and d; it consisted of a copper rod (diameter = 12.5 mm, length = 40 cm). To reduce helium consumption, the copper lead was cooled with liquid nitrogen, and was embedded in a stainless steel dewar. A 40 mm diameter copper flange connected the copper and HTS part of the lead.

The number of tapes was chosen with regard to the limitation of the available current source, which was 880 Amperes. If the upper end of the tapes were at 77 K, the critical current of the lead would be 600 A (= 25 A x 24 tapes). However, this is a worst case scenario; the design of the metal lead should ensure that the temperature at the upper end of the tapes (which is 10 cm below the bottom of the nitrogen dewar) is considerably lower than 77 K. This was confirmed with the tests described in the next chapter.
Fig. 5.2.1: Schematic sketch of HTS current lead (left; without tube) and holder disks (right) for clamping of HTS tapes

Fig. 5.2.2 a: HTS lead with HTS tapes and voltage leads mounted, steel tube detached
Fig. 5.2.2 b: Detail of Fig. 5.2.2 a: end piece of HTS lead, with voltage leads
5.2.2 c: Copper lead with liquid nitrogen (LN$_2$) dewar
5.2.2 d: HTS and copper lead
5.2.2 Test Results

a) Test in liquid nitrogen

As a preliminary test, the HTS lead was tested while fully submersed in liquid nitrogen. This is a worst case scenario for the lead when operating in a helium dewar, where all parts of the lead should be at temperatures below 77 K. Fig. 5.2.3 shows the current-voltage characteristics in LN$_2$ of the various parts of the lead.

The voltage drop across the HTS tape showed an ohmic component, due to the soldered contacts between the tapes (see Fig. 5.2.4). The superconducting-normal transition onset occurred at circa 200 A, consistent with I$_c$ measurements on single tapes ($\approx$ 25 A for each of the 8 tapes). Two 1cm pieces at the high temperature end of the HTS tapes (see Fig. 4), where 24 tapes were placed, show no voltage drop up to 300 A. All other (non-superconducting) parts of the lead showed low ohmic voltage drops below 1 mV. Up to 300 A, all voltages were stable and reproducible, no ‘thermal runoff’ or quench was observed.

Also shown in Fig. 5.2.3 is the current-voltage curve U(I,77 K) of the copper flange connecting the HTS and metal leads. It was tested separately, up to 880 A, where the voltage drop was U(880 A) = 2.8 mV.
b) Test in helium dewar

For the main test of the lead a helium dewar was re-designed. The test setup is shown in Fig. 5.2.4 and 5.2.5 a,b. Due to time limitation only one HTS lead was constructed. A return lead was designed and manufactured, consisting of copper braid in a stainless steel tube (length = 1 m, diameter = 25 mm). The commercial copper braid consisted of 'Pure Annealed Copper Wire', but accurate specifications for purity and low temperature resistivity were not available. The effective conductor cross section was 48 mm². According to Wilson [1], the optimum current (where heat leak per current Q/I is at minimum) for this lead was 1250 A. However, this value is very sensitive to the purity of the copper (which in this case was unknown). For the connection between the HTS and return lead, the same copper braid was used. A voltmeter with a multiplexer was
used to perform these measurements. Eleven voltage taps were connected, and the voltage measured across various parts of the leads, as shown in Fig. 5.2.4.

![Schematic view of lead test setup with positions of voltage taps (A - K)](image_url)

**Voltmeter Channels and Connections:**

<table>
<thead>
<tr>
<th>Ch.</th>
<th>Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>Taps</td>
</tr>
<tr>
<td>1</td>
<td>A - H   (all)</td>
</tr>
<tr>
<td>2</td>
<td>A - B   (Cu lead)</td>
</tr>
<tr>
<td>3</td>
<td>B - C   (Cu flange)</td>
</tr>
<tr>
<td>4</td>
<td>C - D   (conn. to HTS)</td>
</tr>
<tr>
<td>5</td>
<td>D - E   (HTS tape [54 cm])</td>
</tr>
<tr>
<td>6</td>
<td>E - F   (conn. to HTS)</td>
</tr>
<tr>
<td>7</td>
<td>F - G   (Cu braid)</td>
</tr>
<tr>
<td>8</td>
<td>G - H   (return lead)</td>
</tr>
<tr>
<td>9</td>
<td>D - I   (HTS tape [1 cm])</td>
</tr>
<tr>
<td>10</td>
<td>J - K   (HTS tape [1 cm])</td>
</tr>
</tbody>
</table>

Fig. 5.2.4: Schematic view of lead test setup with positions of voltage taps (A - K)
Fig. 5.2.5 a: side view of test setup with HTS, copper and return lead assembled on holder frame
Fig. 5.2.5b: Top view of Test assembly with 1) HTS current lead, 2) return lead, 3) return current lead terminal, 4) nitrogen relief valve, 5) He inlet, 6) current lead terminal, 7) He recovery pipe, 8) LN$_2$ inlet, 9) He pressure gauge, 10) He level meter, 11) voltage terminal
Fig. 5.2.5c: Test setup fully assembled with helium dewar, Current source, voltmeter and He level meter
After the leads were placed into the dewar, the dewar was precooled with liquid nitrogen overnight. The nitrogen was then pumped out with He gas. Finally, liquid helium was filled into the dewar, with the initial He level about 10 cm above the lower end of the leads.

Current-voltage curves were measured up to 880 A, as shown in Fig.s 5.2.6 and 5.2.7. For currents above 600 A, the current could only be switched on for a few seconds, due to heating of the cables connecting the source with the leads. Within these limitations, the leads worked without any problems of quenching or other instability.

The voltage along the entire HTS lead at 880 A was $U(880\, \text{A}) \approx 4\, \text{mV}$, and along the LN$_2$ cooled copper lead $U(880\, \text{A}) \approx 10\, \text{mV}$, while the voltage drop along the return lead was found to be $U(880\, \text{A}) \approx 40\, \text{mV}$ The inset to Fig. 5.2.7 shows the current-voltage characteristics along the entire length (54 cm) of one of the HTS tapes. As in the 77 K measurement, a small voltage drop (180 $\mu$V at 880 A) was measured, stemming from the contacts between the tapes.

The voltage measured along 1 cm pieces at upper end of HTS tapes was zero at all currents up to 880 A. With 77 K at upper end, the ‘critical current of the HTS part would be 600 Amps. This implies that the upper end of the tapes had a temperature considerably lower than 77 K (cf. the discussion in the previous chapter). The same conclusion was derived from considering the voltage drop along the copper flange. It was found to be 1.5 mV at 880 A. This is only around half the value measured at 77 K, and therefore it can be concluded that the upper end of the HTS lead had a temperature much lower than 77K.

The voltage drop at return lead, $U(880\, \text{A}) \approx 40\, \text{mV}$, was a factor of two smaller than the voltage expected at the optimum current, i.e. the optimum current would be 1800 A and the return lead was oversized by a factor 2. This would, of course, lead to an
excess heat leak. The heat leak was determined by measuring the drop of the He level, which is a rather inaccurate method. At zero current,

\[ \frac{\Delta V}{\Delta t} = 2.2 \text{ (±0.5) litres/hour} \]

was found and after applying a DC current: \( I = 500 \text{ A for 10 min} \)

\[ \frac{\Delta V}{\Delta t} = 6.6 \text{ (±1.5) litres/hour} \]

The measured heat leak was double of optimized values for metal leads (Chapter 2.2 and [1]):

\[ P_{\text{opt}} = 2 \times 1.04 \text{ W/kA} \rightarrow \]

\[ (\frac{\Delta V}{\Delta t})_{\text{opt}} = 2.9 \text{ litres/hour at 1000A} \]

\[ (\frac{\Delta V}{\Delta t})_{\text{opt}} = 1.1 \text{ litres/hour at 0A} \]

The excess heat leak was to be expected, because

1) the return lead was oversized by a factor of two.

2) high purity silver was used in the tapes of the HTS lead.

For practical purposes, HTS tapes with alloyed sheath must be used. Apart from this, the conducting properties of the HTS lead were found to be fully satisfying up to the test limit of 880 Amperes. The non-superconducting parts of the lead showed only 4 mV at the current limit, the design of the lead allows upgrading the current capacity by adding more HTS tapes. The actual current limit of the HTS lead could not be determined. It was estimated to be in the range of 5000 A DC.
Fig. 5.2.6: Results of current lead test in helium dewar; results of HTS lead (ch. 3-6) are shown expanded in Fig. 5.2.7

Fig. 5.2.7: Results of HTS current lead test in helium dewar; insert: current - voltage curve of HTS tape
5.2.3 Summary

A novel high $T_c$ current lead, utilizing silver-sheathed Bi2223 tapes, was developed and tested, which allows addition or removal of individual, vapour cooled tapes, thus adjusting the current capacity and optimizing the heat leak per current. Minimum heat leak was obtained by tapering the lead, using more tapes at the high temperature end. To date, the leads have been tested using applied currents up to 900 A DC. However, they are designed for a current capacity of several kA.

References

5.3 General Design Formula for tapered current lead made of N superconducting tapes

It was shown in Chapter 2 that the heat leak of a normal metal current lead cannot be reduced by tapering the lead, due to the coupling of thermal and electrical resistivity via the Wiedemann-Franz law [1,2]. Therefore, metallic leads are usually made with constant cross section, and tapered leads have received little theoretical attention [1]. However, in the case of high temperature superconductor (HTS) leads, tapering can reduce the heat loss, and is practically feasible due to the strong $J_c(T)$ dependence of HTS (Fig. 5.1.6 and 5.1.12).

Ideally, one would choose the cross section $A$, such that along the length of the lead it was described by equation 5.3.1:

$$I_c = J_c(T) / A(T) = \text{const} \quad (5.3.1)$$

For silver-sheathed HTS tapes, this is not possible, as one has to work with discrete cross sections of tapes. The question that needs to be addressed is, how long should each tape in the stack be, in order to minimize the heat leak at maximum current.

In this chapter, a general formula is constructed to answer this question.

1) For a single tape with cross section $A$, length $L$ and critical current $I_c(T)$ at temperature $T$, the current capacity is the critical current at the highest temperature $T_H$, where the critical current is at minimum (Fig. 5.1.6), represented by equation 5.3.2:

$$I_{(1)\text{max}} = I_c(T_H) \quad (5.3.2)$$
2) For a stack of 2 tapes with $L_1 = L$, $L_2 < L_1$, and identical critical currents $I_c(T)$ and cross sections $A$, the current limit depends on the length of the second tape. The maximum possible current capacity is given by

$$I_{(2)_{\text{max}}} = 2 I_c(T_H) \quad (5.3.3)$$

To minimize the heat leak at maximum current capacity, the second tape should be just long enough to ensure that at its lower end the other tape carries $I_{(2)_{\text{max}}}$:

$$I_c(T_2) = 2 I_c(T_H) \quad (5.3.4)$$

where (cf. Fig. 5.3.1)

$$T_2 = T(x_2) = T(L-L_2) \quad (5.3.5)$$

Note that the temperature distribution is changed by the second tape, i.e. it is a function of $L_2$. (The contact resistance between the tapes is neglected).

3) For $N$ tapes in a stack (Fig. 5.3.2), the solution is analogous: the length $L_n$ of the $n$-th tape has to be chosen such that

$$(n-1) I_c(T_n) = N I_c(T_H); \quad n = 2,3,...,N \quad (5.3.6)$$

The temperatures $T_n$ can be obtained from $I_c(T)$ measurements. However, for practical design purposes, the sizes $L_n = L - x_n$ for all tapes are required.
In order to find a formula \( x_n(T_n) \), we consider the heat transfer equation

\[
q = A(x) \kappa(T) \frac{dT}{dx} \quad (5.3.7)
\]

in the section between \( x_n \) and \( x_{n+1} \):

\[
q_n = n A_0 \kappa(T) \frac{dT}{dx}, \quad n = 1, \ldots, N \quad (5.3.8)
\]

where \( \kappa(T) \) is the thermal conductivity, and \( A_0 \) the cross section of the silver sheath alone, which even in silver alloys has a much higher thermal conductivity compared to the HTS core. Through integration from \( x_n \) to \( x_{n+1} \):

\[
q_n (x_{n+1} - x_n) = n A_0 \int_{x_n}^{x_{n+1}} \kappa(T) dT, \quad n = 1, \ldots, N \quad (5.3.9)
\]

which can be written as

\[
q_n (x_{n+1} - x_n) = n A_0 [K(T_{n+1}) - K(T_n)], \quad n = 1, \ldots, N \quad (5.3.10)
\]

with

\[
K(T) = \int_{T_{\text{low}}}^{T} \kappa(T')dT'. \quad (5.3.11)
\]
**CHAPTER 5.3: GENERAL DESIGN FORMULA FOR TAPERED HTS LEADS**

\[ x_{N+1} = L; \quad T_{N+1} = T_H. \]  

(5.3.12)

By limiting our consideration to conduction-cooled current leads only, by definition

\[ q_n = q = \text{const}. \quad \forall \text{ } n = 1, \ldots, N \]  

(5.3.13)

Substituting for \( q \), we can sum eq. (5.3.10) over \( m = 1 \ldots N \):

\[
q (x_{N+1} - x_N + x_N - x_{N-1} + \ldots - x_2 + x_2 - x_1)
= A_0 \left\{ N \left[ K(T_{N+1}) - K(T_N) \right] + (N-1) \left[ K(T_N) - K(T_{N-1}) \right] + \ldots
+ \ldots + 2 \left[ K(T_3) - K(T_2) \right] + K(T_2) - K(T_1) \right\}
\Rightarrow q (x_{N+1} - x_1) = A_0 (N K(T_{N+1}) - K(T_N) - \ldots - K(T_1))
\Rightarrow qL / A_0 = NK(T_H) - \sum_{m=1}^{N} K(T_m) \]  

(5.3.14)

In the same way, by summing eq. 10 from \( m = 1 \ldots n \), we can deduce an equation for tape \# n:

\[
x_{n+1} / A_0 = nK(T_{n+1}) - \sum_{m=1}^{n} K(T_m) \]  

(5.3.15)

Substituting \( x+1 \rightarrow x \) in equation 15 and dividing equation 5.3.15 by equation 5.3.14 yields equation 5.3.16:

\[
\frac{X_n}{L} = \frac{(n-1)K(T_n) - \sum_{m=1}^{n-1} K(T_m)}{NK(T_H) - \sum_{m=1}^{N} K(T_m)} \]  

(5.3.16)

Equation 5.3.16 can be used to calculate the optimum length \( L_n = L - x_n \) of each tape in a stack of \( N \) tapes, and equation 5.3.14 determines the total heat leak characteristics of the optimized tape. Temperatures \( T_n \) are defined by equation 5.3.6, and experimentally determined from \( I_c(T) \) measurements on single tapes. Alternatively, if only \( I_c(77 \text{ K}) \) data are available, one can use empirical \( I_c(T) \) equations found in the literature, e.g. by Kusevic et al. [3], who derived equation 5.3.17:
\[ I_c(T) = I_c(0) \left(1 - \frac{T}{T_c}\right)^{1.4} \quad (5.3.17) \]

Thermal data \( K(T) \), described by Eq. 5.3.11, can be found in the literature for silver [4] and silver alloys [5]. The integrated thermal conductivity is very sensitive to impurity concentration or alloy composition.

For example, in the case of two tapes with \( T_{\text{low}} = 4 \text{ K} \), \( T_{\text{high}} = 77 \text{ K} \), \( T_2 = 60 \text{ K} \), we find that for high purity silver (data from Ref [4])

\[ \frac{L_2}{L_1} \approx 0.05, \]

but for a silver - gold (1 at\%) alloy (data est. from Ref. [5])

\[ \frac{L_2}{L_1} \approx 0.50. \]

The corresponding heat leak is much lower in the second case.

Interestingly, it follows that when a lead has been optimized for, say, 2 tapes, one would, by adding a third tape with \( L_3 < L_2 \) (and not changing \( L_2 \)), decrease the critical current of the lead (because \( T(x_2) \) would increase).

For the lead described in the previous chapter, i.e. groups of three tapes and \( T_2 = 60 \text{ K} \), \( T_3 = 43 \text{ K} \), eq. (16) with the data of Ref. [4] / Fig. 5.3.3 yields

\[ \frac{L_2}{L_1} \approx 0.17 \quad \text{and} \]

\[ \frac{L_3}{L_1} \approx 0.08. \]

These results were utilized in the leads described in Chapter 5.2.
Summary

An analytical model for optimizing the length of HTS tapes in a tapered current lead was derived. A general equation to calculate the heat leak was given. Numerical results obtained for different sheath alloys used in the tapes showed that the optimum length is extremely sensitive to alloy composition.

References


6. Summary and Conclusions

The scope of this thesis was (i) to contribute to the optimization of Bi2223 precursor powder and tape processing and (ii) to develop HTS current leads using Bi2223 tapes.

Two variations of Bi2223 powder stoichiometry were investigated. The first was the copper content and the second, the Bi/Pb ratio. The stoichiometric changes were interdependent and led to quite dramatic changes in the tape microstructure. Increasing the copper content increased the formation of cuprates, while an increased Bi/Pb ratio resulted in increased formation of Bi2201. The most significant change, however, was the increase in the Bi2223 grain size with increasing Bi/Pb ratio. Only small variation in critical currents was observed, but the potential benefits of increasing the Bi2223 grain size by varying the Bi/Pb stoichiometry could be large. The importance of Bi2223 grain size was further demonstrated in a comparison of three commercial powders, which showed that the critical current density increased with increasing Bi2223 grain size. An inverse relationship between the Bi2223 formation rate and the grain size was found. The correlation between the Bi2223 formation rate, grain size and final critical current value was further confirmed by comparing two ‘home-made’ powders which had a different reactivity. One of the powders was heat treated in a low ppO2 atmosphere. This led to the formation of Pb-rich Bi2212, and a much faster Bi2223 formation rate. However, the grain size and final critical current values were larger in the reference tape made from the same powder sintered in air. Investigation of tapes, quenched after various sintering times, showed that a slower Bi2223 formation allowed for the recrystallization of Bi2212. Bi2212 grains were shown to act as templates for Bi2223 growth, and therefore the overall Bi2212 morphology and grain size determine the final Bi2223 morphology.
Various aspects of powder processing have been investigated. It was shown that spray-drying of powders led to better homogeneity compared to co-decomposition. The powder calcination temperature was systematically investigated, and a sequence of 3-4 calcinations at 800 - 820 °C, with intermediate grindings was shown to yield optimum powder properties. Powder grinding, both by hand and in a planetary ball mill, was found to be hampered by absorption of moisture and agglomeration of powder particles. Future work should investigate the possibility of grinding in vacuum or inert atmosphere.

Addition of silver particles to the ceramic core had been reported in the literature to have little effect on $J_c$. In this thesis it was shown that the silver particle size is a crucial factor. The addition of small (5 μm) particles results in a slight reduction of the critical current (perhaps due to the degradation of Bi2223 texture along the spherical silver particles). Large (400 μm) particles were deformed into long flat filaments, which were able to act as templates for Bi2223 growth, leading to better grain alignment, grain density and phase purity of Bi2223 along these layers. By this method, the critical current could be increased by up to 60 % in self-field, and even more in an external magnetic field. Magnetization measurements revealed that the critical current at low temperatures (5 - 20 K) and high magnetic fields (> 2 T) was lower in silver-doped samples. This indicates that the intrinsic pinning properties were changed through silver addition, and needs further investigation.

Large silver particles were also used as a 'tracer' of the powder flow during mechanical deformation. A non-uniform, wavy powder flow was observed even at early stages, before the onset of 'sausaging' at the interface. A parameter study showed that the formation of 'sausaging' in rolled HTSC/Ag tapes depended on the parameters of the deformation process, especially the strain rate, but not on the starting conditions of the tape itself. Based on these findings, a semi-quantitative theoretical model was developed.
The overall density of the oxide core increased only in the early stages of the rolling schedule. A causal relationship between the density and the interface distortion, which has been claimed in the literature, was not confirmed. Instead, it was demonstrated that 'sausaging' is linked to necking and shear band formation: phenomena well known in the classical deformation of metals. This resemblance appears to be a key to a fundamental understanding and control of 'sausaging', and needs to be further explored.

Some other defects related to the silver sheath were also identified. Cracks in the silver at the interface, contamination of the silver with Si and Al, and blistering during heat treatment were all found to have a negative influence on the final tape properties.

It was shown that a two step sintering process can strongly improve critical current density in Bi2223 tapes, attributable to the removal of Bi2201 in the annealing step at 820°C in a two step sintering cycle. The detrimental effect of Bi2201 on J_c was attributed to its non-superconducting nature, plate-like morphology and distribution along Bi2223 colony boundaries, forming blockages to the current flow. A comparison and combination with slow cooling, which was utilized by other groups, revealed that both methods essentially had the same effect. However, the two-step process is preferable, because it allows a 'pin-point' adjustment of the optimum phase composition (for example, avoidance of the '3221' phase). It was shown that the optimum temperature of the second step varies between tapes made from different powders. Some doubt remains on whether the two-step and slow-cooling processes also improved the flux-pinning properties in Bi2223 tapes. More detailed magnetic measurements are needed to clarify this point.

Several Bi2223 growth mechanisms were identified, and shown to compete during tape sintering. Two new mechanisms were shown to exist: epitaxial growth of
Bi2223 on Bi2212 templates and ‘solid state intergrowth’. The latter was proposed to be
the predominant mechanism in the bulk of the core.

Two sets of current leads were developed and tested, both based on the following
design principles:

- vapour cooling of HTS tapes
- maximum flexibility of current capacity (and optimum heat leak per
current Q/I) by allowing exchange of individual tapes

The first pair of current leads was developed for a Superconducting Magnetic
Energy Storage test facility at Monash University. The conducting tapes were held by
plastic clamps and encapsulated in a steel frame. The leads were successfully tested up to
200 A in the stray field of the SMES coil, with no ohmic loss found along the
superconducting parts. The second lead design was aimed at a current capacity of
2000 A. Here, the HTS tape were held by steel clamps in a circular arrangement,
allowing vapour cooling and exchange or addition of individual tapes. In order to reduce
heat losses, the leads were tapered by adding more tapes at the high temperature end,
taking into account the strong $J_c(T)$ dependence. The leads were successfully tested
using applied currents up to 900 A DC. However, their current capacity is estimated to
be several kA. In both cases, Bi2223 tapes with high purity silver sheaths were used, and
consequently the heat loss was high. For practical applications, tapes with alloyed sheath
will have to be used. In the future, the second generation of HTS current leads may be
used for SMES research at Monash University in a system with upgraded power input.

In a theoretical treatment, an analytical model for optimizing the length of HTS
tapes in a tapered current lead was derived, and a general equation to calculate the heat
leak was given. Numerical results obtained for different sheath alloys used in the tapes
showed that the optimum length is extremely sensitive to alloy composition.