Fabrication and characterisation of Bi-2223 current lead

Xuekui Fu

University of Wollongong
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Fabrication and characterisation of

Bi-2223 current lead

A thesis submitted in fulfilment of the requirements for
the award of the degree
Doctor of Philosophy
from
University of Wollongong

By
Xuekui Fu, M. Eng and B. Sci.

Institute for Superconducting and Electronic Materials
&
Department of Materials Engineering
Faculty of Engineering
Year 2001
I, Xuekui Fu, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting & Electronic Materials and the Department of Materials Engineering, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Xuekui Fu

November 2001
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Abstract

This thesis mainly concentrates on (1) developing a novel process for fabricating Bi-2223 bulk current leads, which has big potential to improve the critical current density $J_c$ and contact resistivity of two end terminals, (2) in particular, developing a technique of combining cold isostatic pressing (CIP) and sinter forging which was first used to prepare Bi-2223 bulks and evaluating it with respect to electro-magnetic properties and microstructure features, (3) preparing a prototype of Bi-2223 bar currents. Properties related to technical applications, such as $J_c$ performance and contact resistivity were studied. Grain texture, which has consistently been considered one of the important factors affecting superconducting properties, was quantitatively studied.

A novel technique of combining CIP and sinter forging was applied to the fabrication of Bi-2223 bulks, and pre-sintering was carried out after CIP (route 1) and before CIP (route 2). The effects of the sinter forging deformation rate and pre-sintering were investigated. When the pre-sintering was done after CIP (route 1), the $J_c$ of bulks at 77 K was much higher than that of bulks made by route 2 (pre-sintering was carried out before CIP). Measurements of the field dependence of the $J_c$ revealed that optimised sinter forging could improve $J_c$ behaviour in external fields, particularly in the low field region below 50 mT, for the samples where CIP was carried out before pre-sintering. A higher sinter-forging deformation rate can improve the flux pinning force when the external field is parallel to the sample surface, but degrade the pinning force density when the external force is perpendicular to the sample surface ($H//C$, 77 K).

The influence of the sinter-forging rate on $J_c$ behaviour ($J_c$) in an external field and on contact resistance $R_c$ for prototype Bi-2223 current leads with two silver contact ends
was investigated. The results revealed that $J_c$ was strongly affected by the sinter forging deformation rate and reached a maximum of 725 A/cm$^2$ at a deformation rate of 80% without post annealing. From the measurements of external magnetic field dependence on $J_c$, it was determined that sinter forging could improve $J_c$ behavior in external fields, particularly in the regime below 50 mT. Results showed that the contact resistance was approximately $\sim 10^{-6}$ $\Omega$ cm$^2$ and for the samples with higher deformation rates it became less dependent on the transport current over a range from 0.5 A to 50 A.

The electro-magnetic properties of Bi-2223 current leads after post annealing, with a $J_c$ of 1000 A/cm$^2$ at 77K and in a self-generated magnetic field, were investigated. The texture and weak link behavior were studied by pole figures and AC susceptibility, respectively. The results showed that the matrix density, grain connectivity and texture of Bi-2223 current leads were improved significantly by sinter forging.

Critical currents $I_c$ were measured at 77 K by varying an external DC magnetic field (B), which was applied parallel and perpendicular to the bulk sample surface, i.e., $I_c$ (B//bar surface) and $I_c$ (B$L$bar surface), respectively. The $I_c$ and $J_c$ were 119 A and 300 A/cm$^2$, respectively, for the current lead bar of 0.4 cm thick, 1.0 cm wide, and 5.4 cm long. The effective grain misalignment angle, $\varphi_{\text{eff}}$, was around 10°, calculated from its $I_c$ (B//bar surface) and $I_c$ (B$L$bar surface) curves by using a 2D model. For comparison, the average grain misalignment angle, $\varphi_{\text{av}}$, found in the microstructure using SEM, was measured by pole figure. The results obtained were in agreement with the effective grain misalignment angle $\varphi_{\text{eff}}$. 
However, this is just the beginning of research and development of this proposed new technique for fabricating Bi-2223 bar current leads. Further study and development are definitely necessary; this is because there is much room for improvement, particularly for the processing parameters for each step of this technique.
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Chapter 1: Review of high-$T_c$ superconductors and Bi-2223 bulk current leads

1.1 Fundamental property of Bi-based superconductors

1.1.1 Introduction

There are three high transition temperature families, Y-based, Tl-based, Bi-based, Hg-based and recently discovered MgB$_2$ superconductors. The Bi-Sr-Ca-Cu-O superconducting family has attracted much research due to its promising technical application aspects. There is a series of Bi$_{2}$Sr$_{2}$Ca$_{n-1}$Cu$_n$O$_{2n+4+y}$ compounds in the Bi-Sr-Ca-Cu-O system. The best known compounds with $n = 1$ to $3$ are Bi$_2$Sr$_2$CuO$_{6+y}$ (Bi-2201), Bi$_2$Sr$_2$CaCu$_2$O$_{8+y}$ (Bi-2212) and Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+y}$ (Bi-2223). Superconductivity in the Bi2201 system with a relatively low critical temperature $T_c$ was discovered by Michel et al. [1]. Maeda et al. first reported superconducting transition temperatures between 80 K and 110 K in the Bi-Sr-Ca-Cu-O system, for Bi2212 and Bi2223 phases [2]. All the above mentioned superconductors possess one common feature, that is, their superconducting properties arise from two-dimensional CuO$_2$ planes. For a specific Bi-based system, the $T_c$ increases with an increasing number of CuO$_2$ layers in a unit cell. It should be noted that $T_c$ depends not only on the number of CuO$_2$ layers in a unit cell but is also a function of the doped carrier density (holes) in every CuO$_2$ plane. The four common high $T_c$ families are listed in table 1.1. A new binary superconductor with $T_c$ of 40 K was discovered in year 2001 [14]. This new material has attracted strong attention and has been studied intensively in world wide.
Table 1.1 Y-based, Tl-based and Bi-based superconductors and their $T_c$

<table>
<thead>
<tr>
<th>Family</th>
<th>Compound composition</th>
<th>Abbreviation</th>
<th>$T_c$ (K)</th>
<th>References</th>
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<tr>
<td>Y-based</td>
<td>YBa$_2$Cu$_3$O$_7$</td>
<td>Y-123</td>
<td>90</td>
<td>[3,4]</td>
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<td></td>
<td>YBa$_2$Cu$_4$O$_8$</td>
<td>Y-124</td>
<td>80</td>
<td>[5]</td>
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<td>Y$_2$Ba$_4$Cu$<em>7$O$</em>{15}$</td>
<td>Y-247</td>
<td>60</td>
<td>[6]</td>
</tr>
<tr>
<td>Bi-based</td>
<td>Bi$_2$Sr$_2$CuO$_6$</td>
<td>Bi-2201</td>
<td>20</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>Bi$_2$Sr$_2$CaCu$_2$O$_8$</td>
<td>Bi-2212</td>
<td>85</td>
<td>[2]</td>
</tr>
<tr>
<td></td>
<td>Bi$_2$Sr$_2$Ca$_2$Cu$<em>3$O$</em>{10}$</td>
<td>Bi-2223</td>
<td>110</td>
<td>[7]</td>
</tr>
<tr>
<td>Tl-based</td>
<td>Tl$_2$Ba$_2$CuO$_6$</td>
<td>Tl-2201</td>
<td>80</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>Tl$_2$Ba$_2$CaCu$_2$O$_8$</td>
<td>Tl-2212</td>
<td>105</td>
<td>[9]</td>
</tr>
<tr>
<td></td>
<td>Tl$_2$Ba$_2$Ca$_2$Cu$<em>3$O$</em>{10}$</td>
<td>Tl-2223</td>
<td>125</td>
<td>[10]</td>
</tr>
<tr>
<td>Hg-based</td>
<td>HgBa$_2$CuO$_4$</td>
<td>Hg-1201</td>
<td>75</td>
<td>[11]</td>
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<tr>
<td></td>
<td>Hg$_1$Ba$_2$Ca$_1$Cu$_2$O$_6$</td>
<td>Hg-1212</td>
<td>93</td>
<td>[12]</td>
</tr>
<tr>
<td></td>
<td>Hg$_1$Ba$_2$Ca$_2$Cu$_3$O$_8$</td>
<td>Hg-1223</td>
<td>130</td>
<td>[13]</td>
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<tr>
<td>MgB$_2$</td>
<td>MgB$_2$</td>
<td>MgB$_2$</td>
<td>40</td>
<td>[14]</td>
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</table>

The structure of the Bi-compounds can be viewed as a stack of CuO$_2$ layers interleaved with Ca layers and BiO layers and sandwiched between SrO layers. The three layered phases ($n = 1,2,3$) have very similar energies of formation [15], preventing creation of a single phase (free of stacking faults) in the Bi-Sr-Ca-Cu-O bulk materials. For instance, the $n = 3$ phase is always contaminated by $n = 2$ and $n = 1$ phases. A study of the chemical substitution or chemical doping in the system is important for understanding the origin of
the structure modulation in the Bi-phases, for synthesising new phases and for understanding the superconductivity mechanism. Significant improvement in the stability of the n = 3 phase is observed with the partial substitution of Bi by Pb [15].

1.1.2 Crystal Structures of Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{2n+4+y}$ (n=1, 2, 3) compounds

The crystal structures of Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{2n+4+y}$ (n = 1, 2, 3) are described below. Bi-2201 phase (Fig.1.1.1) has a pseudo-tetragonal symmetry with lattice parameters $a = b \approx 5.4$ Å and $c = 24.4$ Å [16]. The unit-cell of Bi-2201 contains four formula units and is a stack of atomic planes in the sequence (BiO)$_2$/SrO/CuO$_2$/SrO/(BiO)$_2$/SrO/CuO$_2$/SrO/(BiO)$_2$. Bi-2212 phase (Fig. 1.1.2) has a pseudo-tetragonal structure with lattice parameters $a = b \approx 5.4$ Å and $c = 30.8$ Å [17]. The unit-cell of Bi-2212 contains four formula units and is a stack of atomic planes in the sequence (BiO)$_2$/SrO/CuO$_2$/Ca/CuO$_2$/SrO/(BiO)$_2$/SrO/CuO$_2$/Ca/CuO$_2$/SrO. Bi-2223 phase also has a pseudo-tetragonal symmetry with lattice parameters $a = b \approx 5.4$ Å and $c = 37$ Å [1]. The unit-cell of Bi-2223 contains four formula units and is a stack of atomic planes in the sequence (BiO)$_2$/SrO/CuO$_2$/Ca/CuO$_2$/Ca/CuO$_2$/SrO/(BiO)$_2$/SrO/CuO$_2$/Ca/CuO$_2$/SrO.

The structures of Bi-2201, Bi-2212 and Bi-2223 are similar, and the difference between them is in the number of Ca/CuO$_2$ block layers. The block layers containing Sr, Ca, Cu and O, for example, SrO/CuO$_2$/Ca/CuO$_2$/SrO in Bi-2212, have a structure of the perovskite type, and they are responsible for the transport of supercurrent. The SrO/(BiO)$_2$/SrO block layer has a structure of the NaCl type, and is a charge reservoir. The modulated structure arises due to the mismatch of NaCl-type layers to the perovskite-type...
Chapter 1: Review of high-\(T_c\) superconductors and Bi-2223 bulk current leads

layers [18]. Bismuth compounds are susceptible to structural defects such as vacancies, interstitial substitutions, including interstitial oxygen, inter-growths and stacking faults.

Fig. 1.1.1 Crystal structure of Bi\(_2\)Sr\(_2\)CuO\(_{6+y}\) (Bi2201) [17]

Fig. 1.1.2 Crystal structure of Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+y}\) (Bi-2212) [17]
Fig. 1.1.3 Crystal structure of Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+y}$ (Bi-2223) [17]

The typical atomic positions for Bi-2201, Bi-2212 and Bi-2223 unit-cells are given in Table 1.1.1, Table 1.1.2 and Table 1.1.3, respectively [17].
Table 1.1.1 Bi-2201 structure: symmetry and positions of ions [17].

<table>
<thead>
<tr>
<th>Atoms</th>
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<th>y</th>
<th>z</th>
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<tr>
<td>Bi</td>
<td>8l</td>
<td>m</td>
<td>0</td>
<td>0.2758</td>
<td>0.0660</td>
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<tr>
<td>Sr</td>
<td>8l</td>
<td>m</td>
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<td>0.2479</td>
<td>0.1790</td>
</tr>
<tr>
<td>Cu</td>
<td>4e</td>
<td>2/m</td>
<td>1/2</td>
<td>3/4</td>
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<tr>
<td>O1</td>
<td>8g</td>
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Table 1.1.2 Bi-2212 structure: Symmetry and positions of ions [17].

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Table 1.1.3 Bi-2223 structure: Symmetry and positions of ions [17].

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<td>1/2</td>
<td>0.11</td>
</tr>
<tr>
<td>O3</td>
<td>4e</td>
<td>4mm</td>
<td>0</td>
<td>0</td>
<td>0.16</td>
</tr>
<tr>
<td>O4</td>
<td>4e</td>
<td>4mm</td>
<td>1/2</td>
<td>1/2</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Typical X-ray diffraction patterns of Bi-2201, Bi-2212 and Bi-2223 were presented by A. Maeda [19]. The intensity and h, k, l indexes, for Bi-2201, Bi-2212 and Bi-2223 are given in references [20, 21, 22].
1.2 Review of development status of bulk current leads and the sinter-forging techniques

1.2.1 Status for the existing high-\(T_c\) current leads

High-\(T_c\) current leads have attracted considerable attention as a prospective replacement for conventional leads, because of their low thermal conductivity and high critical current density [23]. HTS ceramic current leads are superior to the conventional copper current leads in practical applications for two reasons:

1. Superconducting materials have no electric resistance when they are operating at a temperature below their critical temperatures in DC field. Conventional conductors produce some heat from their electric resistance. Also, the heat increases with increasing current. However, superconducting materials do not generate heat with increasing current, when the materials are in the superconducting state.

2. Bi-2223 ceramics have much lower thermal conductivity. Thin copper tubes or wires are generally used for current leads that supply electric current to a superconducting magnet at cryogenic temperatures. The two ends of each current lead work at different temperatures. Some heat thus transfers from the warm end to the cold end. The thermal conductivity integral from the cold end to the warm end is a critical property. Conventional copper current leads produce a large heat leakage of about 1 W/kA at room temperature through a current lead even in the case of an optimized gas-cooled lead, because copper has a high thermal conductivity. This heat leakage occupies a great part of the total heat leakage in a superconducting magnet system.
Figure 1.2.1 shows the temperature dependence of the thermal conductivity and the thermal conductivity integral for electrolytic copper, phosphorous deoxidised copper and Bi-2223 bulk [24]. For a Bi-2223 ceramic superconductor, the thermal conductivity integral from 4.2 K to 77 K is 1.3 W/cm, which corresponds to 1/3 that of stainless steel, and about 1/40 and 1/500 that of phosphorus deoxidized copper and electrolytic copper, respectively.

Fig. 1.2.1 Comparison in thermal conductivity and thermal conductivity integral at low temperature for electrolytic copper, phosphorous deoxidized copper and Bi-2223 bulk [20]. The two dotted lines refer to the thermal conductivity and thermal conductivity integral, as indicated by two arrows.
Bi-2223 bulks have very low thermal conductivity compared with other high temperature bulks superconductors. Fig. 1.2.2 shows the temperature dependence of thermal conductivity for different high-Tc superconducting bulks. The YBCO tube and rod have higher thermal conductivity, compared with Bi-based 2212 and Bi-2223 rod. The thermal conductivity of Bi-2223 rod is the lowest of all over the range of 0 to 300 K. For example, it is 0.5 W/m•K at 4.2 K, 1.4 W/m•K at 77 K and 2.5 W/m•K at 270 K for Bi-2223 rod [19].

Fig. 1.2.2 Temperature dependence of the thermal conductivity for different high temperature superconducting tubes and rods [19].
The two properties mentioned above are important for practical applications, because they reduce heat leakage during operation. There are four high Tc (i.e. critical temperature) current lead candidates:

1. YBCO material, with a Tc of 90 K, and an excellent Jc \( \sim 10^4 \) A/cm\(^2\) at 77 K [24]. Nevertheless, the material is brittle with severe cracking, and this problem is especially serious for long bulks such as current leads.

2. Melt casted Bi-2212 current leads, with the best Jc \( \sim 10^4 \) A/cm\(^2\) at 77 K. The disadvantage is that the Tc is the lowest at 85 K [25].

3. Bundled Bi-2212 and Bi-2223 tapes or wires, whose best Jc value is \( \sim 10^4 \) A/cm\(^2\) at 77 K [26]. In this case, there is a problem with the high thermal conductivity associated with the silver sheaths.

4. Bi-2223 bulk material, with a Tc of 107 K and the best Jc \( \sim 10^3 \) A/cm\(^2\) at 77 K [27].

Even though Bi-2223 bulk has a low Jc, it has the highest Tc, together with good mechanical properties and easy formability [28] compared to other high temperature superconductors. That is why Bi-2223 current leads are widely chosen for practical applications [29, 30]. However, if the critical current density of Bi-2223 current leads can be improved up to \( \sim 10^4 \) A/cm\(^2\), this material definitely becomes the strongest candidate for technical applications.

Table 1.2.1 is the summary of overall properties for the existing high temperature bulk current lead candidates. These results were released in 1993, so the values of critical current density are much lower than the ones referenced above. It shows that Bi-2223 bulk has a higher Tc, reasonable critical current density, a low thermal conductivity...
integral and a low ratio of the thermal conductivity integral to the critical current density. Besides these strengths, Bi-2223 bulk has the advantages of easy formability, high chemical stability and lower toxicity [31].

Table 1.2.1 A comparison of the overall properties for high-\(T_c\) bulk current lead candidates [31].

<table>
<thead>
<tr>
<th>Candidate</th>
<th>(T_c (K))</th>
<th>(J_c (10^2 A/cm^2) (77K, 0T))</th>
<th>(S_k (w/m) (4\rightarrow77K))</th>
<th>(S_k/J_c (\muWm/A) (77\rightarrow4K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi(2223)</td>
<td>107</td>
<td>12.0</td>
<td>130</td>
<td>10.8</td>
</tr>
<tr>
<td>Bi(2212)</td>
<td>85</td>
<td>6.0</td>
<td>103</td>
<td>17.2</td>
</tr>
<tr>
<td>Y(123)</td>
<td>91</td>
<td>35</td>
<td>1100</td>
<td>31</td>
</tr>
</tbody>
</table>

1.2.2 Existing methods for fabrication of high - \(T_c\) current leads

Different fabrication technologies have been developed to synthesise different high-\(T_c\) current lead candidates. The existing methods for high-\(T_c\) current lead fabrication are the following:

(1). Melt-texturing for YBCO current leads: Melt texturing of the \(\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\) \(\text{YBCO}\) compound results in a superconductor with a layered microstructure of thin \(123\) plates stacked in the \(c\) direction. Several melt-texturing techniques have been developed, such as Melt-Texture-Growth (MTG) [32], Melt-Powder Melt Growth (MPMG) [33], Powder Melt Process (PMP) [30], and Quench and Melt Growth (QMG) [34]. However, all the above processes involve the melting of \(\text{Y123}\) above its peritectic
temperature, $T_p$. When $Y_{123}$ is heated above $T_p = 1015 \degree C$, it melts into a solid $Y_{211}$ phase and a liquid phase according to the reaction:

$$123 (YBa_2Cu_3O_{7-x}) \rightarrow 211 (Y_2BaCuO_3) + \text{Liquid phase}$$

On subsequent slow cooling of the semi-solid melt below $T_p$, oriented $Y_{123}$ grains form with $Y_{211}$ inclusions randomly distributed through the superconducting matrix. The reason some residual $Y_{211}$ phase produced is that some liquid phase is lost during the reaction.

Melt texturing of $Y_{123}$ was first performed by Jin et al [10], who termed this technique as Melt Texture Growth (MTG). In Fig.1.2.3 (a), the corresponding thermal profile is illustrated. The pre-sintered stoichiometric $Y_{123}$ specimen is partially melted at $1020 \degree C \sim 1200 \degree C$. The specimen is then solidified in the presence of a temperature gradient of $20 \sim 50 \degree C/cm$ using a cooling rate of approximately $12 \degree C/h$ until the specimen has reached $350 \degree C$. Soon afterwards, Salama [35] et al. discovered that slow cooling from peritectic temperatures is essential in obtaining large oriented $123$ grains in the form of stacked plates. The thermal profile of Melt Powder Melt Growth (MPMG) is shown in Fig. 1.2.3 (b). In this method, a pre-sintered Y-rich and Y-Ba-Cu-O specimen is rapidly heated to approximately $1450 \degree C$ where the sample decomposes into $Y_2O_3 + \text{Liquid}$. The specimen is then quenched to room temperature and ground into powder. The powder is subsequently pressed into a green body, and rapidly heated to $1100 \degree C$ in air and held at this temperature for roughly 20 minutes. During this holding period, the homogeneously dispersed fine $Y_2O_3$ particles are converted to evenly distributed small $Y_{211}$ precipitates. The specimen is rapidly cooled to $1000 \degree C$ and then slow cooled at a rate of $1-5 \degree C/h$ to approximately $940-950 \degree C$ before cooling to room temperature.
Fig. 1.2.3 Thermal profile of various melt-texturing techniques for Y123 (a) MTG and (b) MPMG [28, 29].

(2). Melt Casting Process (MCP) for Bi-2212 current leads [36]: The oxides are melted in the stoichiometrical ratio of Bi: Sr: Ca: Cu = 2:2:1:2 together with SrSO₄ (preferably about 10 % in weight) at temperatures between 1000 °C and 1200 °C until a homogeneous melt is obtained. The heating process should be as short as possible in order to minimize contamination from the aluminum or platinum crucible. The melt is then poured into copper molds, where it solidifies and slowly cools down to room temperature. The as-cast material consists of a coarse-grained multiphase mixture which also contains a eutectic of CuO₂ and alkaline earth bismuth. A subsequent annealing step between 750 °C and 850 °C generally transforms the compact cast pieces into the pure Bi-2212 phase. The heating conditions depend on the individual thickness of the bulk lead. For the purpose of improving the contacts of MCP Bi-2212 bulk tubes or rods, metal sheets of silver are bent into rings with a diameter equal to the outer diameter of the superconducting parts and fixed in the molds before casting.
The melt (1000 °C) is then poured into the mold, making contact with the silver metal. After annealing, a cross-sectional view exhibits a rugged surface of silver and some 2212 crystallites grown into the soft metal, indicating that a strong interaction occurred during the annealing step. One advantage of MCP is that the process leads directly to three-dimensional formed parts of arbitrary shapes and sizes with comparatively high current density.

(3) Bundled Bi-2223 tapes or wires as current leads: The powder-in-tube (PIT) method was used for Bi-2223 tapes or wires [37]. Appropriate amounts of raw material powders of oxides and carbonates were mixed and calcined at around 800 °C for about 20 hours, packed into a silver tube, drawn to a round wire, then rolled or pressed into a flat tape. The tape was then sintered at 830 ~ 840 °C for 100 to 200 hours in air with one or two intermediate rollings or pressings. Multifilamentary wires were fabricated by stacking silver-sheathed round wires into a silver-tube by single- or double-stacking techniques. These composites were then drawn into round wires and made into tapes. The tapes were encapsulated in steel and held in place by screwed plastic clamps. The steel frame provided mechanical protection as well as a guide for helium vapor. While the lower part of the lead contained HTS tapes as conductor, the high temperature part was equipped with copper braid. The HTS tapes and copper braid were connected with soft solder [38].

(4) Bi-2223 bulk current leads: Cold isostatic Pressing (CIP) was used for Bi-2223 current lead fabrication [39, 40]. The Isostatic pressing implies that the pressure is applied equally in all directions. To fabricate Bi-2223 bulk current leads, five kinds of oxide powders Bi$_2$O$_3$, PbO, SrCO$_3$, CaCO$_3$, and CuO, were weighed out to obtain an ion ratio of (Bi+Pb): Sr: Ca: Cu = 2:2:2:3, ground, and calcined. The calcined powder
was then packed into a rubber mold and formed into a bulk tube or rod by cold isostatic pressing at a pressure of 400 MPa [39]. The bulk was sintered for 100 hours at 810 – 840 °C in an atmosphere of low oxygen partial pressure (Ar:O₂ = 12:1), and then the CIP process was repeated again. Finally, silver powder was plasma sprayed to form silver layers on both ends of the bulk tube for current contacts, and the tube was sintered again. The bulk tubes range from 10 mm to 30 mm in inside diameter in 5 mm steps, 1.2 mm to 1.4 mm in wall thickness, and 200 mm in length. The plasma-sprayed silver layers extended 20 mm from each end [39, 40].

The transport critical current (Ι_c) and critical current density (J_c) of the bulk tubes and rods measured with a dc four-probe method at 77 K under self-magnetic field is shown in Table 1.2.2. For all of the bulk tubes, the transport critical current density exceeds 1000 A/cm². The Ι_c of the bulk tubes increases proportionally with an increase in the cross-sectional area. The Ι_c of the bulk rod with a diameter 7 mm, is about half that of the bulk tubes; also, the J_c tends to decrease with increasing the diameter of the rod. The T_c values of the bulk tubes and rod are about 108 K. The overall contact resistance including the plasma–sprayed silver layer and the soldered portion on it is about 0.1 – 0.2 μΩ at 77 K, and the values fall one order of magnitude at 4.2 K [39, 40].

Fig 1.2.4 shows the magnetic field dependence of J_c at 77 K for Bi-2223 bulk tube, varying the applied current and the direction of the applied field with respect to the current flow. The J_c decreases with increasing applied magnetic field. The J_c drops to half at an applied field of 20 mT perpendicular to the current flow and 40 mT parallel to the current at 77 K. At 4.2 K, the J_c values are one order of magnitude higher than
those at 77 K. For instance at 4.2 K, $J_c$ is about 7000 A/cm$^2$ at 100 mT and 3800 A/cm$^2$ at 500 mT with the field perpendicular to the current in both cases.

The previous fabrication methods, Melt-texturing and Melt Casting process, are not suitable for the fabrication of Bi-2223 current leads, because of the complicated multiple phase decomposition of Bi-2223 if the temperature applied is higher than the melting-point temperature [41]. The CIP technique does not result in highly textured and well contacted grains. Also, the existing method for preparing extended terminals results in coating layers on the two terminal surfaces, and the coating contacts become worse after cycling several times from low temperature to room temperature. All existing methods for the fabrication of high-$T_c$ current leads are summarised in Table 1.2.3.

Table 1.2.2. $I_c$ and $J_c$ of Bi-2223 bulk under self-field at 77 K [42]

<table>
<thead>
<tr>
<th>O.D × I.D × length (mm)</th>
<th>$I_c$ (A)</th>
<th>$J_c$ (A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.6 × 10 × 200 (tube)</td>
<td>520</td>
<td>1130</td>
</tr>
<tr>
<td>17.6 × 15 × 200 (tube)</td>
<td>730</td>
<td>1100</td>
</tr>
<tr>
<td>22.4 × 20 × 200 (tube)</td>
<td>900</td>
<td>1240</td>
</tr>
<tr>
<td>7.0 × 200 (rod)</td>
<td>220</td>
<td>570</td>
</tr>
</tbody>
</table>
Fig 1.2.4 Magnetic field dependence of transport $J_c$ of sintered Bi-2223 bulk at 77 K and 4.2 K [42].

1.2.3. Sinter-forging technique for small pellet specimen fabrication

Sinter forging was applied to the fabrication of small pellets of both Bi-2212 and Bi-2223 materials as early as 1988 by K. Kugimiya et al. [50]. The green compacts were isostatically pressed and then a slip casting of the flakes under pressure or sinter forging was applied. After sintering again, the compacts contained materials with a $T_c$ of 80 K (for Bi-2212) and 110 K (for Bi-2223) as proved by the Meissner effect. However, the critical current and critical current density were not reported in Kugimiya’s paper.
Table 1.2.3 Fabrication methods for high-\(T_c\) current leads

<table>
<thead>
<tr>
<th>Existing Method</th>
<th>Bi(2223) /Best (J_c)</th>
<th>Bi(2212) /Best (J_c)</th>
<th>Y(123) /Best (J_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid Reaction</td>
<td>(\sim10^2) A/cm(^2) [42]</td>
<td>(\sim10^2) A/cm(^2) [43]</td>
<td>(\sim10^2) A/cm(^2) [44]</td>
</tr>
<tr>
<td>Melt-texturing*</td>
<td></td>
<td></td>
<td>(\sim10^4) A/cm(^2) [45]</td>
</tr>
<tr>
<td>CIP + Sintering*</td>
<td>(\sim10^3) A/cm(^2) [46]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sinter-forging**</td>
<td>(\sim10^4) A/cm(^2) [47]</td>
<td>(\sim10^4) A/cm(^2) [48]</td>
<td></td>
</tr>
<tr>
<td>Melt Casting Process*</td>
<td></td>
<td></td>
<td>(\sim10^4) A/cm(^2) [49]</td>
</tr>
</tbody>
</table>

*Used for current lead fabrication

**Sinter-forging has only been used to fabricate Bi-2223 small samples

Followed Kugimiya’s work, other groups began to fabricate Bi-based superconducting samples using the sinter-forging technique. N. Murayama et al. also reported their results in 1989 [51]. The processing details are as follows: superconducting ceramic powder \((T_c = 105\) K) with the starting composition of Bi\(_{0.85}\)Pb\(_{0.15}\)Sr\(_{0.8}\)CaCu\(_{1.4}\)O\(_y\) was prepared by a solid-state reaction. The powder was then uniaxially sinter-forged at a pressure of 300 kg/cm\(^2\) at 830 °C in air for 2 hours in a cylindrical die made of alumina. The samples were annealed in air or \(O_2\) gas. The 105 K phase with a nominal composition of Bi\(_{0.85}\)Pb\(_{0.15}\)Sr\(_{0.8}\)CaCu\(_{1.4}\)O\(_y\) was changed to a phase with \(T_c < 100\) K or a nonsuperconducting phase by sinter-forging in air, although no appreciable change in X-ray diffraction patterns was observed. After annealing at
830 °C in air for 80 hours, the critical current density was 656 A/cm² at 77 K, which was an order of magnitude higher than that of normal sintered samples [51].

In 1991, the sinter-forging technique was applied to fabricate Bi-2223 thick films. It was reported that the technique was effective in significantly improving critical current density. N. Murayama first fabricated Bi₁.₈₄Pb₀.₃₄Sr₂.₀₃Ca₁.₉₇Cu₃.₀₆Oᵧ thick films by the sinter-forging method [52]. The thick films were prepared on MgO substrates by screen printing with the powder consisting almost entirely of 110 K phase. The film was sandwiched between two MgO substrates and then sinter-forged in air under various conditions. The thickness of the film was 20 ~ 40 μm. When the temperature was 855°C under a pressure of 500 kg/cm² for 3 hours, the critical current density Jₐ reached a maximum value of 9500 A/cm² at 77 K, and the critical temperature was 110 K. It is noted that when the sinter-forging pressure was higher than 200 kg/cm², the degree of the grain orientation was almost independent of the pressure, but the critical current density increased with increasing sinter-forging pressure.

B. M. Moon et al. studied the effects of sinter-forging on the 110 K phase formation, grain texture, and bulk density for the Bi-2223 bulk samples [53]. The starting Sb-doped powder with a nominal composition of Bi:Pb:Sb:Sr:Ca:Cu = 0.8:0.16:0.04:1.0:1.0:1.4 was mixed by ball milling, then dried for 24 hours at 120 °C, calcined in air at 780 °C for 12 hours, reground, and calcined at 820 °C for 6 hours. Some powders were pressed into pellets using a pressure of 2000 psi. The specimens were then sintered in air at 865 °C for 120 hours using heating and cooling rates of 2 °C/min. Sinter-forging was carried out for both calcined powders and pre-sintered pellets using a pressure of 4.5 MPa and a temperature of 861 °C for 5 hours under
flowing oxygen, and then the pressure was decreased to 1 MPa at 861 °C for 20 hours. The magnetic transitions as a function of temperature were measured for sinter-forged samples before and after annealing at 860 °C for 115 hours in air. The sinter-forged samples with calcined powder appeared non-superconducting down to 80 K, indicating that the Bi-2223 phase was not present. However, after annealing at 860 °C for 115 hours a sharp transition appeared at 110 K with large amounts of the Bi-2223 phase being formed. Sinter-forged samples from the pre-sintered pellet exhibited a Meissner effect starting at 110 K, but the transition was notably broad. After annealing at 860 °C for 115 hours a slightly sharper transition was observed in the magnetisation curves. One of the sinter-forged samples was found to be above 90% of the theoretical density. However, after annealing at 860 °C the bulk density decreased slightly. The decrease was explained by anisotropic growth of the superconducting crystalline phases [53].

The process behavior during sinter forging is actually very complicated, and was addressed by some researchers. N. Murayama et al. [55, 56] studied the mechanism of sinter-forging behavior for Bi-2223 bulks densification. In his experiment, green Bi-2223 bulks were prepared by uniaxially pressing in a specially designed die. The starting powders with a nominal composition of Bi₁.₈₄Pb₀.₃₄Sr₂.₀₃Ca₁.₉Cu₃.₀₆O₇ were prepared by a solid-state reaction, then uniaxially cold-pressed at 19.6 MPa. The compact body was then hot pressed in a temperature range of 780 °C ~ 840 °C and pressure range of 4.9 MPa ~ 24.5 MPa in air for 2 hours, and was finally cooled to room temperature at a rate of 160 °C/h. The die was made of aluminum, and the inside surface of the die was coated with MgO powder in order to prevent a reaction between the superconductor and the die. From the relationship between the degree of grain orientation and the relative density, the degree of grain orientation is large when the
relative density is lower than about 90% as shown in Fig. 1.2.5. This indicates that particle rearrangement often takes place when the relative density is lower than 90%.

The relationship between porosity, p, and hot pressing conditions was formulated as [56]:

\[ \ln(p) = -\alpha_0 \exp\left(-\frac{E}{RT}\right)P + \ln(p_0) \]

where \( P \) was the hot-pressing pressure, \( p_0 \) the porosity of the compact body, \( E \) an apparent activation energy, \( T \) the temperature, \( R \) the gas constant, and \( \alpha_0 \) a constant.

The apparent activation energies for densification were 184 KJ/mol and 526 KJ/mol in the temperature ranges above and below 820 °C, respectively [56]. In summary, the densification behavior for this material seems to be well described in terms of plastic flow, particle rearrangement, and the presence of a liquid phase. In the low temperature range below 820 °C, particle rearrangement seems to be the main mechanism for the densification. In the higher temperature range, plastic flow seems to be the main mechanism. The mass density after hot-pressing increased remarkably to higher than 90 % of theoretical density (6.35 g/cm³), when the temperature of the hot pressing was above 820 °C, regardless of the hot-pressing pressure. The highest value achieved was 99.7 % of theoretical density at 840 °C with a pressure of 19.6 Mpa [56].

The phase transformation during the sinter-forging was systemically studied by N. Murayama et al. They reported that sinter-forging caused a unique phenomenon in the decomposition of (Bi, Pb)-2223 phase is unique phenomena because the side surface of a sample is free during the sinter-forging [39]. The raw oxides were mixed, fired and ground repeatedly. The sintering schedule was 750 °C for 5 hours, 800 °C for 5 hours, 850°C for 20 hours and 850 °C for 50 hours in air. The bulks with a nominal composition of \( \text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{2.03}\text{Ca}_{1.9}\text{Cu}_{3.06}\text{O}_y \) were sinter-forged at a temperature range
Fig. 1.2.5 Relationship between the degree of grain orientation and relative density for hot-pressed samples [55].

of 840 °C to 870 °C and under a pressure of 9.8 Mpa in air for 20 hours. At high temperature, Bi-2223 phase decomposes into (Sr,Ca)$_2$CuO$_3$ phase and liquid phase,

$$(\text{Bi,Pb})_{2223} \rightarrow (\text{Sr,Ca})_{2}\text{CuO}_3 \text{ phase} + \text{Liquid phase}$$

where the liquid phase has a composition between the 2201 phase and 2212 phase. The decomposition of the (Bi,Pb)$_{2223}$ phase is rapid in normal sintering at high temperature, as the liquid phase co-exists with the (Bi,Pb)$_{2223}$ phase. However, in the case of sinter-forging at high temperature, the (Bi,Pb)$_{2223}$ phase decomposed to (Sr,Ca)$_2$CuO$_3$ phase and liquid phase, followed by the extrusion of liquid phase from the inner part to the outer part of the samples due to the uniaxial pressure. Therefore,
Chapter 1: Review of high-Tc superconductors and Bi-2223 bulk current leads

the decomposition of the (Bi,Pb)-2223 phase in the sinter-forging was slow compared to normal sintering. The critical current density increased with increasing sinter-forging temperature. It is noted that the sample sinter-forged at 870 °C had the highest Jc in spite of having the highest content of (Sr,Ca)2CuO3 phase. The high temperature heat treatment during the sinter-forging has both positive and negative effects on critical current density. The positive effect relates to the grain growth and the improvement of grain coupling. The negative aspect is the formation of large grains of (Sr,Ca)2CuO3 phase. The resultant Jc of sinter-forged samples is determined by the above two factors. The values of Ic and Jc of the sample sinter-forged at 870 °C were 71 A and 2350 A/cm² a 77 K. Fig. 1.2.6 shows the sinter-forging temperature dependence of the area of a typical grain of the (Sr,Ca)2CuO3 phase and the fraction of the (Sr,Ca)2CuO3 phase, which is calculated by binary image analysis on back scattered electron (BSE) images. These values increased remarkably above 860 °C [57]. In another paper [58], it was reported that residual defects existed near sub-grain boundaries in the Bi-2223 grains. The generation and propagation of dislocations along the a-b plan due to bending stresses during the sinter-forging result in the formation of sub-grain boundaries. The disorder near sub-grain boundaries is relieved by a short period of heat treatment. This is another reason for the observed increase in Jc. It was found that the application of uniaxial pressure alone was not totally effective for improving grain orientation in dense Bi-2223 samples and that uniaxial pressure caused the sub-grain boundaries resulting in a decrease in Jc. These results suggest that grain orientation should be accomplished before densification in order to achieve high-Jc bulk superconductors [59].
A. Tampieri et al [60, 61, 62] studied the effects of precursor powder preparation methods, starting compositions (essentially based on variation of the Ca/Sr ratio) and sinter-forging parameters on the critical current density performance. It was concluded that the process phenomenology is strictly linked to the powder starting stoichiometry: when the composition is very near to the theoretical (2223) values, secondary phase extrusion is observed during sinter-forging, yielding a purification and inhibition of (2212) formation accompanied by an appreciable increase of $J_c$. On the other hand, when the Ca/Sr ratio is considerably greater than one and the Cu excess is low, recrystallization of (2223) from the liquid takes place, with a remarkable improvement in $J_c$.

Fig. 1.2.6 Average area of one grain of $(\text{Sr,Ca})_2\text{CuO}_3$ phase and the fraction of $(\text{Sr,Ca})_2\text{CuO}_3$ phase as a function of sinter-forging temperature for (Bi,Pb)-2223 samples. The uniaxial pressure and sinter-forging time were 9.8 Mpa and 20 hours, respectively.
in the critical current density ($J_c > 10^4 \text{ A/cm}^2$ at 77 K). A sharp increase in the relative density and the orientation factor is obtained when sol-gel powders are employed, but high powder reactivity implies degradation phenomena that hamper transport mechanisms. When using pyrolysed powders, a large increase in the number and dimensions of non-superconducting secondary phase precipitates hinders the texture development. By optimising the preparation procedure for pyrolysed powders and the temperature during the sinter forging, it was possible to increase the texture development, avoiding any secondary phase recrystallization and exceeding $10^4 \text{ A/cm}^2$ in $J_c$ value.

Introducing MgO whiskers successfully reinforced the Bi-2223 ceramic matrix without degradation in superconducting properties. The experimental details for preparing the BSCCO/MgO composite is as follows [63]: BPSCCO intermediate precursor with a nominal composition of $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{2.03}\text{Ca}_{1.9}\text{Cu}_{3.06}\text{O}_y$ was pre-sintered to convert it into highly pure Bi-2223 phase. MgO whiskers, with average diameters ranging from 0.5 to 5 μm and lengths from 50 to 600 μm, were selected as the reinforcement material, based on the excellent thermodynamic and thermo-mechanical compatibility of MgO with BPSCCO matrix [64]. Properly selected amounts of MgO whiskers and highly pure BPSCCO powder were first wet-mixed in isopropyl alcohol for one to two hours. After drying, green composite specimens were formed into a bar shape, and then calcined at 800 °C. Up to three times repeating cycles of sinter forging and annealing were conducted at a temperature of 820 °C with a pressure of 27.6 Mpa. for 2 to 5 hours, then annealing was conducted at 832 °C for 72 ~ 96 hours in an 8% oxygen atmosphere. The BPSCCO/MgO composite obtained demonstrated excellent $J_c$ when the whisker volume fraction was less than 10%. When the fraction was higher than
10%, however, the value of critical current density was reduced. The main reason for the $J_c$ degradation was due to impeded grain growth in the BPSCCO matrix. The dependence of critical current density on the whisker volume fraction in $(\text{MgO})_w$/BPSCCO composite is shown in Fig. 1.2.7. It is revealed that the composite with the highest volume percentage of MgO whiskers has the lowest $J_c$. The $J_c$ decreased slightly with increasing volume fraction $V_w$ when $V_w < 0.1$, but rapidly when $V_w > 0.1$. The $J_c$ degradation was explained by not only the reduction in the superconducting cross-sectional area, but also by the inhibition of grain growth of the BPSCCO phase [65].

The critical current density of Bi-2223 bulks has been significantly improved by optimizing the sinter-forging parameters over the past ten years. In 1988, it was claimed that a critical current density $J_c$ of 656 A/cm$^2$ at 77 K was achieved by introducing optimised sinter-forging [66], which was an order of magnitude higher than that of a normal sinter-forged sample ($J_c < 100$ A/cm$^2$ at 77 K). By the year 2000, the critical current density at 77 K for small Bi-2223 bulk samples had been reported to $10^4$ A/cm$^2$ by several different groups through optimizing the processing, including the starting precursor powder preparation, pre-sintering, sinter-forging, high temperature heat treatment during the sinter-forging and post annealing. A. Tampieri et al. achieved a high critical current density over $10^4$ A/cm$^2$ at 77 K, by properly controlling the starting nominal composition and the sinter-forging cycles [67, 68]. A critical current density with of nearly $10^4$ A/cm$^2$ was also achieved by N. Nurayama et al [69]. From the results, sinter forging with a short heat treatment at 885 °C improved the $J_c$ of the sinter-forged bulk BPSCCO by about 9 times. It was concluded that one of the reasons for the increase in $J_c$ was the disappearance of a Bi, Pb-rich phase and the Bi-2212
Fig. 1.2.7 Effect of the whisker volume fraction on $J_c$ (77K and zero field) in \((\text{MgO})_w/\text{BPSCCO}\) composite processed by 3-cycle sinter-forging and annealing [63].

Phase as observed in scanning transmission electron microscopy. The short heat treatment at 885 °C caused the Bi, Pb-rich phase to decompose to Sr-Ca-Cu-O phases and a phase with the elements Bi and Pb. The latter phase, apparently a liquid phase, was subsequently extruded from the sample by uniaxial pressure. The Bi-2223 phase suffered scarcely any decomposition as the result of a heat treatment at 885 °C in air for 15 min when uniaxial pressure was applied. In 1999, Nurayama et al reported that the best $I_c$ and $J_c$ were 71 A and 2350 A/cm² at 77 K and 0T [70], for a sample with a width of 3 mm and a thickness of 1 mm. The sample sinter-forged at 870 °C had the
highest $J_c$ in spite of having the highest content of (Sr, Ca)$_2$CuO$_3$ phase. The high temperature heat treatment was effective for the improvement of grain coupling.

In summary, the advantage of this technique is that the material is uniaxially pressed at a high temperature that is close to its melting temperature. It is thus an effective method for significantly improving the texture of Bi-2223 material and results in a $J_c$ improvement. The best $J_c$ achieved by this method is $\sim 10^4$ A/cm$^2$ at 77 K [71, 72]. However, this technique, sinter forging, has not been employed to fabricate large bulk samples by other groups working on high-$T_c$ superconductors. Even though, there is no evidence to show that this technique is only restricted to small sample fabrication.

1.2.4 Practical applications of Bi-2223 bulk current leads

Bi-2223 current leads already have technical applications in some superconducting systems, and they are widely employed in different devices. One example of Bi-2223 current lead applications is that they have been successfully used in a cryo-cooler cooled superconducting magnet in Japan [38,39]. The magnet had a diameter of 380 mm, a height of 920 mm, and a weight of 190 kg. It had no liquid helium system. A Ti-added Nb$_3$Sn coil in the magnet was fixed on the second stage of a Gifford-McMahon cryo-cooler for conductive cooling. A pair of Bi-2223 bulk current leads was used in the system. One end of each Bi-2223 lead was connected to the second stage (10 K) of the cryo-cooler, and other end to the first stage (50 K). The cryo-cooler cooled superconducting magnet generated a stable high magnetic field of 4 Tesla for 96 hours without cryogen. This magnet had been working for 10,000 hours and had experienced a continuous holding time of 1,200 hours at 370 hours operation and 40 separate quenches for a test. No problems occurred with either the coil or the Bi-2223 bulk
current leads. The current leads also have some applications in other types of superconducting device, such as superconducting magnetic energy storage (SMES) and current limiters [71, 72, 73]. The purpose of SMES is to store electrical energy during off peak hours, and to release it during peak hours.

Bi-2223 current leads with higher critical current densities will have more technical applications, because they have high $T_c$ combined with good mechanical properties and easy formability compared with other high $T_c$ superconductors. However, the low critical current density, $\sim 10^3$ A/cm$^2$ at 77 K, currently restricts their applications. This is because superconductors with low critical current densities will require a larger cross-sectional area to carry the same current, which will introduces a large heat leakage into the high-$T_c$ system.

Replacing conventional current leads with HTS current leads will greatly reduce the maintenance costs for superconducting systems. Because conventional metal current leads have electric resistance, they normally are designed to have a large cross-sectional area to carry the required current. Otherwise, the temperature will build up. However, current leads with a large cross-sectional area conduct more heat from the warm end to the cold end. This requires more cooling liquid, and liquid helium is surprisingly expensive. Maintaining a superconducting system is thus very expensive if conventional current leads are used, because the refrigeration occupies a large proportion of the total cost.
1.3. Techniques of preparation of low resistivity contacts for high-$T_c$ superconductors

1.3.1 Introduction

Preparing high-quality contacts is a very important issue for both critical current measurements and practical applications of high-$T_c$ superconductors. Low quality contacts produce considerable heat causing the superconductors to work in a disturbed state. Obviously, this is a particularly critical parameter for high-$T_c$ bulk current leads, as they transfer large currents and are also directly connected to other superconducting devices, such as magnets, high-$T_c$ cables and superconducting magnetic energy storage (SMES). Contact resistivity is used as a measure of interface quality that is independent of the contact area. It is expressed as $\rho_c = RS$, where $R$ is the contact resistance and $S$ is the contact area [74].

Different applications require different contact resistivities as shown in Fig. 1.3.1. The requirements for contact resistivity $\rho_c$ vary greatly for the three different types of applications – Magnet, electronic package and on-chip interconnects. $\rho_c$ values for magnet applications and for the measurement of critical current must be less than $\sim 10^{-4}$ to $10^{-5}$ $\Omega$-cm$^2$ to prevent unacceptable heat and voltage generation at the current connections. Nominal $\rho_c$ values in the $10^{-8}$ $\Omega$-cm$^2$ range are needed for thin-film package interconnections. However, for on-chip interconnections, contact resistivities less than $10^{-10}$ $\Omega$-cm$^2$ are necessary. Additionally, for superconductor/normal-metal interfaces in Josephson-junction applications, $\rho_c$ values must typically be in the $10^{-11}$
\(\Omega\)-cm\(^2\) range, or lower [74]. The method used to measure contact resistivity is described in the experimental chapter.

Fig. 1.3.1 Overall nominal contact resistivity \(\rho_c\) in \(\Omega\)-cm\(^2\) required for different applications and the types of contacts achieving these levels [75].

1.3.2. Methods for preparing high quality contacts (\(\rho_c = 10^{-5}\) to \(10^{-11}\) \(\Omega\)-cm\(^2\))

To prepare non-critical contacts with \(\rho_c \geq 10^{-3}\) \(\Omega\)-cm\(^2\), the easiest method is to directly solder the lead wires to the superconductor with indium and indium alloy solder. This is because indium-based solders have a melting temperature typically in the range of 120 °C to 160 °C, which is significantly lower than standard eutectic Pb-Sn solder (183 °C). Also, indium-based solders generally wet either bare or silver–sheathed high–T\(_c\) materials. However, it is better to use an ultrasonic soldering iron without any solder flux, avoiding solder flux death problem with most high–T\(_c\) superconductors. The flux wicks into the superconducting materials along grain boundaries and degrades the
grain boundaries and the transport properties of the superconductor. Silver paint, silver paste, or silver-based epoxy can also be used to prepare these non-critical contacts for some delicate applications [75].

In fabricating contacts to high-$T_c$ ceramic superconductors, three problems are encountered: 1. A barrier layer may be formed at the contact interface from the contact material and thus chemically degrade the superconductor surface, 2. The superconductor surface degrades from exposure to air and other processing gases or liquids [76]. The early contact failures are shown in Table 1.3.1. It is revealed that common Pb-Sn solder does not form a bond with YBCO. Silver paint is more strongly attached, but the interface resistivity is still high. Indium produces a contact resistivity $\rho_c$ that is still not low enough for practical applications, even for a contact prepared on a freshly exposed superconductor surface. For example, even when the superconductor surface was cleaned in a vacuum and a Cu or Au /Cr layer immediately bid down, no significant improvement was observed [76].

Table 1.3.1 shown that the difference in contact resistivity $\rho_c$ between the common contact materials and noble metal materials is obviously significant. $\rho_c$ is reduced by more than four orders of magnitude to the $10^{-6}$ $\Omega$-cm$^2$ range. It is noted that oxygen annealing the contact interface is very effective for reducing $\rho_c$ by another four orders of magnitude to below $10^{-10}$ $\Omega$-cm$^2$ [77]. The lowest contact resistivity obtained so far has reached the $10^{-10}$ to $10^{-12}$ $\Omega$-cm$^2$ range using contact methods involving either ultra-high-vacuum (UVH) surface-preparation [78, 79] or co-processing techniques which are carried out simultaneously [80,81].
Table 1.3.1 Summary of contact results for YBa$_2$Cu$_3$O$_x$ [76]

<table>
<thead>
<tr>
<th>Material</th>
<th>Contact resistivity at 76K ($\Omega$-cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common contact materials (Unannealed)</td>
<td></td>
</tr>
<tr>
<td>Pb-Sn</td>
<td>No bond</td>
</tr>
<tr>
<td>Ag paint</td>
<td>$10^{-1}$ to $10^{0}$</td>
</tr>
<tr>
<td>In solder (scratch under solder)</td>
<td>$10^{-2}$ to $10^{-1}$</td>
</tr>
<tr>
<td>In solder (2% Ag) (ultrasonically soldered)</td>
<td>$10^{-2}$ to $10^{-1}$</td>
</tr>
<tr>
<td>Cu (sputtered)</td>
<td>$10^{-2}$</td>
</tr>
<tr>
<td>Au/Cr (sputtered)</td>
<td>$10^{-1}$</td>
</tr>
<tr>
<td>Noble-Metal contacts (annealed)</td>
<td></td>
</tr>
<tr>
<td>Ag (sputtered)</td>
<td>$10^{-6}$ to $10^{-5}$</td>
</tr>
<tr>
<td>Au (sputtered)</td>
<td>$10^{-6}$ to $10^{-5}$</td>
</tr>
</tbody>
</table>

The fact is that most contact materials may work well for normal conductors, but cannot produce high quality contacts on high-$T_c$ oxide superconductors. One complicated method has been found for solving the problems mentioned above. It has three steps:

1. Clean the superconductor surface.
2. Use a noble metal for the contact material.
3. Anneal the noble metal/superconductor interface in oxygen.

The first step must be carried out if the superconductor surface is not fresh or has been contaminated with other materials. Up to now, no contact material other than a noble metal has been proven to result in high quality contacts. Sometimes the third step can
be omitted if the surface preparation in the first step is of high quality [81, 82, 83].

Generally, these three steps are carried out as separate steps, but they also can be carried simultaneously. The above three basic steps are reviewed in more detail in the following.

1.3.2.1 Superconductor surface preparation

A non-degraded superconductor surface can be prepared by in-situ or ex-situ processing. In the in-situ process, the as-fabricated superconductor surface is protected by a contact buffer layer which is immediately grown on the superconductor surface before exposure to air or other processing [78, 81, 83, 84]. For bulk materials, the superconductor and contact can be co-processed: the contact material is put in contact with the superconductor before heating begins. This method is preferred because it is a simple method that produces excellent contacts. However, in many cases, the in-situ contact process is not compatible with other processing steps that must be conducted before the contacts are prepared. In the ex-situ contact process, the already degraded superconductor surface is etched away, and a noble metal contact is then deposited. This is a simple technique that produces excellent contacts.

1.3.2.2 Selection of contact materials

As noble metals have a low oxygen affinity, they are essential as contact materials for high-\(T_c\) ceramic superconductors [76, 77]. Auger electron spectroscopy (AES) results from the depth profiles of contact interfaces have indicated that the noble metals play an essential role in achieving extremely low contact resistivity [76]. For instance, an AES depth profile for an Ag/YBCO sample was conducted by Ekin et al. with a sputter...
etching rate of around 20 nm/min. There was negligible oxygen in the silver layer, with some inter-diffusion at the interface between the silver and the YBCO.

1.3.2.3 Oxygen annealing

Additional optimized oxygen annealing is sometimes effective for improving the contact resistivity. For example, Ag/YBCO contacts were annealed in oxygen at 600 °C for 1 hour or at a very low temperature of 250 °C. The results show that considerable inter-diffusion of silver occurs in the first case. Silver diffusion through the interface provides low resistivity paths that effectively shunt the degraded interface layer [76]. Similar AES results were obtained for gold/YBCO contacts annealed in oxygen at 600 °C for 1 hour, which show that no oxygen is observed in the gold layer, and annealing leads to diffusion of gold into the YBCO and replenishment of oxygen at the Au/YBCO interface.

1.3.2.4 Lead connections to contact pads

After the noble-metal buffer material has been fabricated on the superconductor, the next problem is how to attach the current bars to the noble metal buffer layer. The fact is that most solders will alloy through thin noble metal buffer layers and react with the high-\(T_c\) superconductor to form an oxide barrier layer. As a result, what has started as an excellent contact is completely degraded by the lead-attachment process [76]. To solve this problem for thin (< 5 μm) noble-metal contact pads requires a careful selection of solder as well as making the noble-metal contact pad thick enough so that reactive solder elements do not alloy through the buffer. For example, Eutectic In-3 % Ag is a good compromise for soldering to thin noble–metal contact pads, because it does not scavenge silver or gold and also has a relatively low melting temperature (143
°C. Indium-based solders are mechanically too soft for forming robust connections, although they are good for keeping the soldering temperature low. Eutectic 52%-48% In-Sn solder is much stronger than pure indium and has a low melting temperature, but it easily alloys with noble metals [84].

1.3.3 Summary of contact fabrication techniques

From a practical point of view, the techniques for preparing contacts can be classified into different categories according to different criteria. For example, they are separated into three main categories, low temperature, medium temperature and high temperature depending on the temperature of contact preparation. From Table 1.3.2, a processing temperature no higher than 100 °C is classified as low temperature, no higher than 600 °C as medium temperature, higher than 600 °C as high temperature. A low temperature is necessary if contact material reactions are to be avoided and if other temperature-sensitive processing steps must be carried out before contacts are made. The high-temperature techniques (≥ 600 °C) require temperatures approaching the sintering or melting temperatures used to fabricate the superconductor in the first place and must be planned and performed early in the processing sequence.

Contact preparation techniques can also divided into two categories according to the sequence of contact preparation. In the post-processing technique contacts are fabricated after the superconducting material is made. This technique has the advantage of processing compatibility, because the contacts are fabricated after superconductor fabrication, in a separate processing step. Co-processing techniques are techniques where the contacts are fabricated at the same time as the superconductor material. These techniques are actually the simplest, because the superconductor
surface is prepared in-situ in the presence of the contact materials. Although simultaneous processing of the superconductor and contact is not always possible for many applications, this technique minimizes the number of processing steps and usually produces high-quality contacts as indicated by research done around the world (Table 1.3.2).
### Table 1.3.2. Summary of contact fabrication techniques

<table>
<thead>
<tr>
<th>Processing temperature (°C)</th>
<th>Contact material</th>
<th>Superconductor</th>
<th>Contact thickness (μm)</th>
<th>Lead attachment</th>
<th>Meas. temp. (K)</th>
<th>Contact resistivity $\rho_c$ (Ω·cm$^2$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low temperature (≤ 100 °C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Sputtered Au film</td>
<td>Sputter-etched sintered YBCO</td>
<td>6</td>
<td>Au-ribbon bond</td>
<td>76</td>
<td>8×10$^{-6}$</td>
<td>[86]</td>
</tr>
<tr>
<td>20</td>
<td>Sputtered Ag film</td>
<td>Sputter-etched sintered YBCO</td>
<td>2.5</td>
<td>Au-ribbon bond</td>
<td>76</td>
<td>7×10$^{-6}$</td>
<td>[86]</td>
</tr>
<tr>
<td>~100</td>
<td>Evaporated Au film</td>
<td>Sputter-etched sintered YBCO</td>
<td>20</td>
<td>solder</td>
<td>77</td>
<td>6×10$^{-6}$</td>
<td>[85]</td>
</tr>
<tr>
<td>20</td>
<td>Sputtered Ag film</td>
<td>Sputter-etched sintered YBCO</td>
<td>1-6</td>
<td>Au-ribbon bond</td>
<td>76</td>
<td>10$^4$ to 10$^{-5}$</td>
<td>[86]</td>
</tr>
<tr>
<td>Medium temperature (≤ 600 °C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500 °C /5h</td>
<td>Evaporated Ag film</td>
<td>Sintered YBCO</td>
<td>20</td>
<td>Solder</td>
<td>77</td>
<td>4×10$^{-8}$</td>
<td>[86, 87]</td>
</tr>
<tr>
<td>Direct wire-Bonds</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500 °C /1h</td>
<td>Ultrasonic-bonded Ag wire</td>
<td>Sintered YBCO</td>
<td>-</td>
<td>50 μm diam. Ag wire</td>
<td>78</td>
<td>3×10$^{-8}$</td>
<td>[88]</td>
</tr>
<tr>
<td>500 °C /1h</td>
<td>Spot-welded Ag wire</td>
<td>Sintered YBCO</td>
<td>-</td>
<td>50 μm diam. Ag wire</td>
<td>78</td>
<td>2×10$^{-7}$</td>
<td>[88]</td>
</tr>
<tr>
<td>Processing temperature (°C)</td>
<td>Contact material</td>
<td>Superconductor</td>
<td>Contact thickness (μm)</td>
<td>Lead attachment</td>
<td>Meas. temp. (K)</td>
<td>Contact resistivity ρc (Ω-cm²)</td>
<td>References</td>
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<tr>
<td>High-Temperature (&gt;700 °C)</td>
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<td></td>
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<tr>
<td>Deposited Noble Metal contacts</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>900 °C</td>
<td>Ag epoxy</td>
<td>Sintered YBCO</td>
<td>-</td>
<td>Ag epoxy glue</td>
<td>77</td>
<td>1×10⁻⁷</td>
<td>[89]</td>
</tr>
<tr>
<td>850 °C /1h</td>
<td>Evaporated Au film</td>
<td>Sintered YBCO</td>
<td>-</td>
<td>In solder</td>
<td>4.2</td>
<td>≤1×10⁻⁸</td>
<td>[89]</td>
</tr>
<tr>
<td>970 °C /0.5h+slow cooling in O₂</td>
<td>Melted Ag beads</td>
<td>Sintered YBCO</td>
<td>~ 1000</td>
<td>Au wire in molten</td>
<td>77</td>
<td>&lt; 1×10⁻⁸</td>
<td>[90, 91]</td>
</tr>
<tr>
<td>Direct wire-bonds</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SC-to-SC contacts</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>910 °C /18h+930 °C /12h</td>
<td>Melted-processed YBCO</td>
<td>Melt-processed YBCO</td>
<td>-</td>
<td>Melt-processed YBCO</td>
<td>77</td>
<td>&lt; 1×10⁻¹⁰</td>
<td>[92]</td>
</tr>
<tr>
<td>High-temperature co-processing techniques</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>950 °C /6h</td>
<td>Embedded Au cylinder</td>
<td>Sintered YBCO</td>
<td>1000 (d)×1000 (h)</td>
<td>In solder</td>
<td>&lt; 20</td>
<td>4×10⁻³</td>
<td>[80]</td>
</tr>
<tr>
<td>920 °C /40h</td>
<td>Embedded Ag-wire</td>
<td>Sintered YBCO</td>
<td>125</td>
<td>In-10%Ag solder</td>
<td>77</td>
<td>&lt;1.6×10⁻¹²</td>
<td>[81]</td>
</tr>
<tr>
<td>Processing temperature (°C)</td>
<td>Contact material</td>
<td>Lead attachment thickness (μm)</td>
<td>Contact thickness (μm)</td>
<td>Superconductor</td>
<td>Measurements</td>
<td>Measurements</td>
<td></td>
</tr>
<tr>
<td>-----------------------------</td>
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<td>------------------------</td>
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<td>--------------</td>
<td>--------------</td>
<td></td>
</tr>
<tr>
<td>1030 °C, cooling with rate 10 °C/h</td>
<td>Embedded Ag wire</td>
<td>Melt-processed</td>
<td>YBCO</td>
<td>Embedded Ag particles</td>
<td>Ag-sheath</td>
<td>Melt-processed</td>
<td>YBCO</td>
</tr>
</tbody>
</table>
| 920 °C/16h | Arc-Spraying Techniques | 25-76 | Sintered Ag | press sheet 100 μm | Pressed sheet 100 μm | - 41 -
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References


Chapter 1: Review of high-Tc superconductors and Bi-2223 bulk current leads


Chapter 2. Experimental Methods

2.1 Introduction

The precursor powders were prepared using the pyrolysis technique described in section 2.2. To fabricate Bi-2223 bulk current leads using the sinter-forging technique, the green bulks must satisfy a length requirement, which is typically 10 to 20 cm. In order to satisfy this requirement, cold isostatic pressing (CIP) was employed to produce long bar green bulks. The pre-sintering of the precursor powders can be conducted before and after CIP pressing. Sinter forging was then carried out at different deformation rates under different pressures and repeated two or three times to get well-textured bulks. Finally, post annealing was carried out on those deformed Bi-2223 bulks. A schematic diagram of the process procedure used for preparing Bi-2223 bulks is shown in Fig. 2.1.

2.2. Precursor powder preparation

The first, and most crucial step in the preparation of high quality Bi-2223 superconductor is the preparation of precursor powders with sufficient purity and homogeneity, as well as the desired phase composition and particle size distribution. The precursor powders were prepared using spray pyrolysis as detailed below. Five oxides, Bi$_2$O$_3$, PbO, SrCO$_3$, CaCO$_3$ and CuO, were weighed accurately according to the stoichiometric ratio of Bi/Pb/Sr/Ca/Cu = 1.72/0.34/1.83/1.97/3.13. The mixture was dissolved in dilute nitric acid, and then the solution was sprayed into a heated chamber, together with nitrogen gas. An aspirator pump created a high-speed gas flow, pumping the resultant powder into a second chamber where the powder was collected. The liquid spray rate, gas flow speed,
and inlet (spray) temperature were carefully controlled. The resultant powder was gradually moved into a preheated furnace, then calcined ~ 780°C to decompose the mixture into oxides. The sintering and grinding were repeated 2 ~ 4 times, until the desired phase composition and homogeneity were reached.

Fig. 2.1 Schematic diagram of the process procedure used for Bi-2223 bulks.
2.3. **Cold isostatic pressing and pre-sintering**

The precursor powders were packed in plastic cylindrical containers with a homogenous mass distribution and were well sealed. Cold isostatic pressing was then carried out at pressures in the range from 200 Mpa to 400 Mpa. The pressed rods were taken from the plastic containers and the pre-sintering was carried out around 850 °C for 100 ~ 200 hours in air. XRD diffraction patterns were taken to determine if the sintering conditions were optimized. This optimization includes the temperature and the total pre-sintering time. Pellets were cut from the rods for the next step, the sinter-forging process.

2.4. **Sinter-forging**

The sinter-forging apparatus is shown in Fig. 2.2. Pellets were inserted into the silver foil and uniaxially pressed inside the vertical furnace. The temperature, pressure and time of each sinter forging were equally critical parameters for large bulk samples, because inhomogeneous deformation and cracks are detrimental to the critical current density. Too much deformation at one time will cause serious cracks in the bulks, so sinter forging was thus repeated several times, applying appropriate pressures.

The deformed long plates were overlapped for the next stage sinter forging, as shown in Fig. 2.3. Pellets were sinter-forged 2 ~ 3 times at 850 °C ~ 870 °C for 25 hours, and their total thickness reduction rates were varied from 0 to 90% by applying different pressures during the process. The temperature of the sinter forging, which should be a slightly lower than the melting point of the Bi-2223 bulks, must be strictly controlled. The reasons are
that higher temperatures will result in melting of the bulks, and the Bi-2223 phase will decompose into other secondary phases, and if the sinter-forging temperature is too low, very hard ceramic bulks are very difficult to deform even if a high pressure is applied during the process. So, the temperature on the sample surface must be checked often and accurately controlled. Four contact terminals to be used for critical current density
measurements were inserted between two overlapping pellets before the last sinter forging.

![Diagram of sinter-forging steps]

**Fig. 2.3** Progress of samples through the sinter-forging steps.

### 2.5. Post annealing

It is found that post annealing can significantly improve the critical current density, as this process can transform some remaining second phases into the Bi-2223 phase. Some of these secondary phases, such as Bi-2201 and Bi-3221, are very detrimental for the critical current density [1-3]. Post-annealing in low oxygen partial pressures with nitrogen gas was conducted in a sealed furnace. Systematic study of the effects of low oxygen/nitrogen atmospheres with different partial $O_2$ pressures and nitrogen content (from 100% to 92.5%) on phase transformation was carried out and is described in chapter 6. XRD
diffraction patterns and SEM images were analyzed to ensure that the post annealing was optimized.

2. 6. Characterization of powders and bulk samples

**Critical current density performance and electromagnetic characterization.** The critical current density, \( J_c = \frac{I_c}{S} \), is the most important property for HTS applications, where \( I_c \) is the critical current and \( S \) the cross-sectional area carrying the current. \( J_c \) is a function of temperature, magnetic field, and other parameters. The standard critical current measurement was carried out with a 1 \( \mu \)V/cm criterion at temperatures from 4.2 K to 77 K. DC current supplies with a limit of around 800 A and voltmeters with a resolution of 0.1 \( \mu \)V were used for the critical current density measurement. Current sources with current limits of 100 A (Hewlett Packard 6672 A) and 875 A (Hewlett Packard 6680A) were available. The standard resolution of the voltmeters (Keithley DMM 196 and Keithley 2000/2001) was 0.1 \( \mu \)V. For determining the magnetic field dependence of the critical current, a 1.2 Tesla magnet. The external field was applied both parallel and perpendicular to the broad surface of the bulk samples. Critical temperatures were determined by AC susceptibility measurements in a Quantum Design Physical Properties Measurement System (PPMS). The PPMS was also used for measuring magnetization loops. From this, the critical current density was calculated using the Bean model and compared with transport critical current density measurement.

**Phase and microstructure analysis.** Because the microstructure and superconducting properties are closely linked, microstructure analysis plays a crucial role in optimizing Bi-
2223 bulk processing. It is not sufficient to measure critical current density or other electromagnetic properties alone. Only microstructure investigation allows us to determine which factor of the material processing limits the critical current density, and which part of the processing needs to be further improved.

Phase and microstructure analysis were carried out using XRD, X-ray texture analysis, SEM optical microscopy, Transmission Electron Microscopy (TEM), differential thermal analysis and thermogravimetric DTA/TG and particle size analysis.

**X-ray diffraction (XRD)** is by far the fastest and most convenient method for phase characterization of Bi-2223 powder and bulk samples. XRD diffraction patterns identify different phases and give a semi-quantitative estimation of the phases. Samples are easily prepared by cracking the bulk samples. Sometimes the bulks need to be ground to fine particles before conducting XRD experiments in order to obtain more accurate results. The relatively high background ‘noise’ 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 1 μm. Therefore very small amounts of secondary phases cannot be detected.

**X-ray Texture Analysis** is a technique, which allows a more accurate determination of the grain alignment using pole figures.

**Scanning Electron Microscopy (SEM)** and **Optical Microscopy** allow direct observation of the microstructures. While the resolution of the optical microscope is limited to approximately 1 μm, the SEM can provide information on the structure in the sub-micron range. An important tool in SEM is **Energy Dispersive Spectroscopy (EDS)**, which can be used to identify the different phases and the stoichiometry. The bulk samples are broken along the direction of their cross section, so, the degree of grain alignment and
grain connection for different samples can be directly observed and compared. If necessary, TEM can be used for studying microstructures with high resolution.

**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 other method. This is because of 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 surface.

Particle Size Analysis (PSA) allows measurements of the particle size distribution of precursor powders. First, the powder is poured into a liquid (commonly water) and the distribution is 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 not accurate because of possible agglomeration of the powders, which could not be separated even with the built-in ultrasonic stirrer.

The bulk density was measured for each processing step. The mass (M) of a bulk was measured on a laboratory balance. The volume (V) was determined by the water displacement method. The mass density was the result of the ratio of the mass of a bulk to its volume; that is, $D = \frac{M}{V}$. 
2.7. Contact resistivity $\rho_c$ measurements

The contact resistance was measured using a four-probe method. The contact resistivity, $\rho_c = \frac{R_c}{S}$, was calculated, where $R_c$ is the contact resistance of the interface between the Bi-2223 ceramics and terminal connectors, and $S$ is the area of the interface.

Figs. 2.4 and 2.5 show the schematic diagrams of the superconductor sample with current and voltage leads for measuring contact resistivity.

Current is injected into the superconductor through one contact pad and extracted from another. Two leads are attached to the current pad to be measured, one for introducing current, and the other for detecting voltage at the surface of the pad. Another voltage tape is attached directly to the superconductor, as close as practical to the current pad (but not touching it). Below the critical temperature $T_c$, the contact resistance $R$ is just the voltage measured between these voltage tapes, divided by the current passed. Sometimes the resistance of the normal-metal pad affects the result, but usually this is small in comparison with the contact resistance. Above $T_c$, the measured value of the contact resistance must be corrected for the resistance of the normal superconductor material between the contact pad voltage tape (marked 1 in the Fig. 2.5) and the second voltage tape (2 in Fig. 2.5) by measuring the resistivity per unit length of the superconductor. This was done using another voltage tape (3 in Fig. 2.5) attached to the superconductor. However, below $T_c$ no correction is needed, as the sample is superconducting.
Fig. 2.4 Four-terminal method for measuring contact resistivity (below $T_c$).

Fig. 2.5 Four-terminal method for measuring contact resistivity (above $T_c$).

The contact area $A$ is the interface area between the superconductor and a contact pad. As the contact is sandwiched between two ceramic bulks, the contact area is the total area of the two contacted sides of the silver sheet (that is $S$), or simply double the value of the area contacted on one side (that is $A$). It is expressed as $S = 2A$. At least three
measurements were conducted on samples having different surface areas to ensure that spreading resistance in the contact pad did not affect the results.

Appendix: Equipment used for chemical, microstructural and electromagnetic analysis

- Particle Size Analysis (PSA)
  Malvern mastersizer
  Range: 50 nm ~ 800 μm

- Differential Thermal Analysis / Thermogravimetry (DTA/TG)
  Setaram TGA 92-16.18
  Scan rate typical 10 C/min; TG resolution 1 μg

- X ray Diffractometer (XRD)
  Philips PW 1730 generator, Philips PW 1050 Goniometer (Θ-2Θ) with graphite monochrometer
  Radiation: Cu K, Filter: Ni

- XRD texture analysis
  Philips PW 1729 generator, PW 1087 Goniometer (φ-χ)
  Radiation: Co

- Scanning Electron Microscope (SEM)
  Leica Stereoscan S440
  LINK Oxford EDS Detector
References


Chapter 3: Preparation and characterization of precursor powders

3.1 Introduction

The quality of the precursor powders is very important to the final properties of superconducting Bi-2223 bulks produced by the sinter-forging technique. The powder quality depends on the following factors: 1. The starting oxide compounds and initial nominal mixing composition for different elements; 2. Techniques and processing parameters used for powder preparation.

Different starting stoichiometric compositions for Bi-2223 used by some companies are compared in Table 3.1. To promote the formation of Bi-2223 phase, PbO is usually added. In a Pb-doped sample, Ca$_2$PbO$_4$ is responsible for accelerating the Bi-2223 phase formation [1].

Table 3.1 Nominal compositions used for Bi-2223 superconductors [2]

<table>
<thead>
<tr>
<th>Companies</th>
<th>Bi</th>
<th>Pb</th>
<th>Sr</th>
<th>Ca</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASC</td>
<td>1.8</td>
<td>0.3</td>
<td>1.9</td>
<td>2.0</td>
<td>3.1</td>
</tr>
<tr>
<td>IGC</td>
<td>1.8</td>
<td>0.4</td>
<td>2.0</td>
<td>2.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Siemens</td>
<td>1.8</td>
<td>0.4</td>
<td>2</td>
<td>2.1</td>
<td>3</td>
</tr>
<tr>
<td>Toshiba</td>
<td>1.72</td>
<td>0.34</td>
<td>1.83</td>
<td>1.97</td>
<td>3.13</td>
</tr>
<tr>
<td>Sumitomo</td>
<td>1.8</td>
<td>0.4</td>
<td>2.0</td>
<td>2.2</td>
<td>3.0</td>
</tr>
</tbody>
</table>

A. Tampieri et al. studied the influences of different starting stoichiometries and different techniques on phase transformation and critical current density [3, 4, 5]. BSCCO (2223)
superconducting powders were prepared by three different techniques, solid, pyrolysis and sol-gel, and with three different stoichiometries (Bi: Pb: Sr: Ca: Cu = 1.84: 0.34: 1.91: 2.03: 3.06, 1.70: 0.30: 1.80: 2.30: 3.10 and 1.70: 0.30: 1.70: 2.30: 3.30), mostly based on variation of Ca/Sr and Cu concentration. Different sinter-forging cycles were then applied to attain higher density and orientation factors. It was concluded that the process phenomenology is strictly linked to the powder starting stoichiometry: when the composition is very near to the theoretical (2223), effects of secondary phase extrusion are observed during sinter-forging, yielding a purification and inhibition of (2212) formation accompanied by an appreciable increase in Jc. As the Ca/Sr ratio is considerably >1, recrystallisation of Bi-2223 from the liquid takes place, with a remarkable improvement in critical current density exceeding $10^4$ A/cm$^2$. As the nominal composition diverges from Bi-2223 with Ca/Sr $>>$ 1 and Cu excess, the formation of too many precipitates of non-superconducting phases hinders the texturing process and degrades the intergranular properties.

Although there are a number of techniques available for the preparation of precursor powders, they can be essentially classified into two types: solid-state reaction and solution routes. The solid-state reaction technique consists of the following steps: mechanical mixing of appropriate amounts of starting materials, then 1 ~ 3 cycles of repeated calcining and grinding. Long sintering times and accurate temperature control are required for this process. Otherwise, large particles of Sr-Ca-Cu-O, Ca-Cu-O and CuO phases are commonly presented in the resultant powders [6, 7].
Chapter 3: Preparation and characterization of precursor powders

The solution route for powder fabrication includes co-decomposition, co-precipitation, spray drying and sol-gel processing, in which the metal nitrates and oxides are dissolved into a solution, dried and calcined. The solution route provides close control of the physical and chemical characteristics with the main advantages being enhanced homogeneity, uniform particle size and close control of stoichiometry. However, special attention should be paid to the precise control of processing parameters, such as the pH values in co-precipitation and sol-gel methods, to avoid severe impurity segregation. The spray drying technique was used for the powder processing in my PhD project.

3.2 Precursor powder preparation

The solution used in this work was prepared by dissolving oxide compounds in a diluted nitric acid with a cation stoichiometry of Bi: Pb: Sr: Ca: Cu = 1.72:0.34:1.83:1.97:3.13. The solution was spray dried using a PULVIS MINI-SPRAY (Model GA-32) Dryer made by Yamato Scientific Co., Ltd.. The system configuration is shown in Fig. 3.1. The solution, which was stirred continuously throughout the process using a magnetic stirrer to maintain its homogeneity, was sprayed via the spray nozzle into the main drying chamber kept at 200 °C. The dried powder was then transported to a cyclonic collector from the main drying chamber by heated air as the carrier gas. The temperature at the outlet of the collector chamber was maintained at about 100 °C throughout the process.

The light blue raw powder was heated slowly to 500 °C at a rate of 3 °C/h, then calcined at 800 °C ~ 820 °C for 5 hours, ground for 1 or 2 hours and re-calcined at 800 °C ~ 820 °C for 8 hours to form a homogeneous mixture with a desirable phase assemblage. To
decrease the particle size and to speed up the reaction rate during powder calcination, the "Pulverisette" FRITSCH planetary mill was used. The resultant compound was called the "spray dried" precursor powder.

Fig. 3.1 Schematic diagram of the spray dryer system

3.3 Characterization of the precursor powders

3.3.1 Particle size distribution
Grinding of powders was conducted between the calcination steps, in order to promote complete reaction and improve homogeneity. As preparing bulk samples needs a large amount of powders, a planetary ball mill with a zirconia jar and balls was used to grind the powders. The total time of each grinding step greatly affects the particle size distribution. Particle size analysis (PSA) was conducted using the Malvern Mastersizer described in chapter 2. \( D_{v, 0.5} \) is the volume median diameter used for describing the particle size distribution. It is directly calculated from the data by the software supplied with the Mastersizer. The particle size analyzer was also equipped with an ultrasonic bath, which was used to break up agglomerations. The particle size and distribution for a series of powders were investigated for each batch of samples.

Fig. 3.2. (a) shows the particle size distribution of the “spray dried” precursor powders after 1 or 2 hours grinding. Powder 1 was ground for 1 hour, and the particle size distribution is bimodal having a mean volume diameter \( D_{v, 0.5} \) of 40.5 \( \mu \text{m} \). After grinding for 2 hours, \( D_{v, 0.5} \) of powder 2 showed a significant decrease to 3.9 \( \mu \text{m} \). It means that sufficient grinding is very necessary for obtaining fine green precursors.

Fig.3.2 (b) shows the volume distribution percentage as a function of particle size for the reacted green precursor powders 3 and 4. The green powders were pressed into discs with a diameter of 2.5 cm, and then sintered in air at 850 °C for 120 hours. The discs were broken and ground separately for 2 hours (powder 3) and 4 hours (Powder 4). The volume median diameters of powder 3 and powder 4 were 19.0 \( \mu \text{m} \) and 9.1 \( \mu \text{m} \).
Fig. 3.2 (a) Particle size distribution of powder 1 (after grinding for 1 hour) and powder 2 (after grinding for 2 hours).
Fig. 3.2 (b) Particle size distribution of precursor powder which was calcined at 850 °C for 120 hours in air, then ground for 2 hours (powder 3); and ground for 4 hours (powder 4).
3.3.2 Differential thermal analysis (DTA) scan data

DTA measurements were conducted to optimize the temperature for further heat treatment and sinter forging. Fig. 3.3 shows two DTA curves for green precursor powders and reacted powders calcined at 850 °C for 120 hours in air. The green precursor has its first onset melting temperature at 836 °C. From its X-ray diffraction (XRD) pattern, the main phase for this green precursor is 2212 phase with other minor phases. This is in good agreement with the B. Zimetz research work results, which showed first onset melting temperature range of 825 °C to 845 °C [8]. The reacted powder has its first melting temperatures around 860 °C, and the main phase is Bi-2223 phase.

3.3.3 Scanning Electron Microscope (SEM) micrographs

SEM allows a more direct observation of particle size distribution and homogeneity. Fig. 3.4 (a) shows SEM image of the green precursor powder 2. Fig. 3.4 (b) shows a SEM image of the reacted powder 3. By comparison, the green precursor powder is composed of small particle sizes below 5 µm and very homogeneous. However, the image of the reacted powder that was ground for 2 hours shows that most particles have a plate-like shape and a variable particle size. Some particles are considerably larger than 5 µm.
Fig. 3.3 DTA curves of the precursor powder and the reacted powder sintered at 850 °C for 120 hours in air.
Fig. 3.4 SEM images of (a) the precursor powder 2 and (b) the reacted powder 3.
3.3.4 X-Ray diffraction (XRD) patterns

In order to get the most reliable results from XRD, all samples were crushed and ground to fine powders for XRD measurements. Fig. 3.5 shows the XRD patterns for a series of precursor powders after different processing steps. Three representative peaks were chosen for comparison of their changes during processing in air. In Fig. 3.5 (a), the XRD pattern was from the original precursor; (b), (c) and (d) XRD patterns were from the precursor powders processed by a series of steps: all three were first cold isostatic (CIP) pressed at 200 Mpa; (b) was sintered at 850 °C for 40 hours in air; (c) was sintered 858 °C for 80 hours in air; and (d) was sintered at 858 °C for 120 hours in air. From XRD spectra, it is clearly seen that precursor powder (a) is a mixture of several phases including Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ (Bi-2212) and Bi$_2$Sr$_2$CuO$_{6+x}$ (Bi-2201). With increasing annealing time, the Bi$_2$Sr$_2$Ca$_2$Cu$_2$O$_{10+x}$ (Bi-2223) phase content increases while the content of the Bi-2212 phase decreases. After annealing for 120 hours in air, the XRD pattern for powder (d) shows predominately Bi-2223 phase with very little Bi-2212 phase.

As seen from XRD pattern (b) in Fig. 3.5 some Bi-2212 phase remained after calcining the powders for 40 hours in air, but it is noted that most of the Bi-2212 phase was transformed into Bi-2223 phase. However, powders (c) and (d) were cold isostatic pressed and sintered for 80 or 120 hours, and their XRD patterns showed very little Bi-2212 phase left in the powders. The high-$T_c$ Bi-2223 percentage was greater than 90%. This indicated that powder treated with cold isostatic pressing (high pressure) is beneficial to the transformation of the Bi-2212 phase into Bi-2223 phase and that the phase transformation is much more rapid than for powder treated with normal cold pressing (low pressure). This implies that good contact between the particles promotes transformation. After further
sintering in air up to 160 hours, the XRD spectra (not included in Fig. 3.5) showed no significant differences from XRD patterns (c) and (d). This indicated that the phase transformation essentially completed by heating the cold isostatically pressed samples at 860 °C for 80 ~ 120 hours.

![XRD patterns](image)

Fig. 3.5 XRD patterns for a series of precursor powders (a) original precursor powder; (b) CIP + 850 °C/40 hours in air; (c) CIP + 858 °C/80 hours in air; (d) CIP + 858 °C/120 hours in air.
3.4 Summary

Bi-2223 precursor powders with overall small particle size (< 5 μm) and homogeneity were successfully fabricated using a spray-drying technique. A nominal composition with a cation stoichiometry of Bi: Pb: Sr: Ca: Cu = 1.84:0.34:1.91:2.03:3.06 was used and proved to be a desirable starting composition. A solution of dissolved oxide compounds was spray dried. In order to homogenize the powder, to decrease the particle size and to speed up the reaction rate during powder calcination, the collected blue raw powder was heated slowly to 500 °C at a rate of 3 °C/h, then calcined at 800 °C ~ 820 °C for 5 hours, ground for 1-2 hours and re-calcined at 800 °C ~ 820 °C for 8 hours. The XRD pattern showed that the original precursor powder was predominately Bi-2212 phase with some minor phases. DTA measurement indicated that the green precursor powder has an onset melting temperature of about 836 °C. SEM images showed that the green precursor powder was composed of small particles with sizes below 5 μm. Particle size analysis (PSA) showed that ‘spray dried precursor powder’ had a mean volume diameter $D_{v, 0.5}$ of 40.5 μm which decreased to 3.9 μm after an additional one hour grinding. This indicated that adequate grinding is very necessary for obtaining fine green precursors.
Chapter 3: Preparation and characterization of precursor powders

Reference


Chapter 4: Effect of pre-sintering and deformation rate on critical current density behavior of Bi-2223 bulk samples made by sinter-forging

4.1 Introduction

Bi-2223 bulk ceramics have been previously considered for use in current leads at low temperature, such as applications in SMES [1, 2, 3] and electrical fault current limiters [4], because it has good superconducting behavior, reasonable mechanical properties at 77 K [5], resistance to environmental degradation and relatively easy workability [6]. Soon after the discovery of Bi-based superconductors, in 1998, sinter forging (or hot pressing (HP) as it is called by some scientists) was employed to improve the critical current density for Bi-based superconductors [7,8]. It was reported that more than 95% of the grains were oriented in the c-axis direction for hot-pressed bulks. Sintered compacts generally contained materials with a $T_c$ of 80 and 110 K as proved by the Meissner effect. Actually, these composites were mixtures of Bi-2212 and Bi-2223 phases [7]. Also, the bulk density of the hot-pressed samples reached as much as 6.21 g/cm$^3$, which was over 95% of the theoretical density, with $T_c$ of 72 K. After annealing at 835 °C in air for 40 h, the $T_c$ improved to 10 K and the critical current density at 77 K was found to be 731 A/cm$^2$ [8]. In 1999, Murayama et al reported that a critical current density of 656 A/cm$^2$ at 77 K had been achieved in sinter forged samples that was annealed at 830 °C in air for 80 h, which was an order of magnitude higher than the $J_c$ of a conventionally sintered sample [9]. Moon et al obtained sinter-forged samples with a majority of Bi-2223 phase, highly
oriented plate-like grains, and high bulk density values [10,11]. Pre-sintered pellets were sinter forged at 861 °C in flowing oxygen with an initial pressure of 4.5 MPa for 3.5 h and subsequently annealed. Grains were elongated with the c-axis oriented approximately parallel to the direction of applied stress. The critical current density at 77 K increased with increasing bulk density [12].

Several techniques have been employed to fabricate Bi-2223 bulks, but sinter forging is the most effective for improving the mass density and grain alignment. Yoo et al. reported that hot isostatic pressing (HIP) is very effective for improving the bulk mass density [13], but it gives little improvement in grain alignment. By using a sequence of Hiping and intermediate cold pressing, high-density Bi-based superconductors of close to 6.15 g/cm³ were produced, which is much higher than conventionally sintered compounds which typically have a density of 3 ~ 4 g/cm³ [13]. HIP can give highly dense, superconducting Bi-2212 and Bi-2223 with only slight decomposition [14], but if Y123 is hot isostatic pressed to full density in a metal capsule, then the nonsuperconducting phase forms as a result of decomposition [14].

Liquid-phase sintering and cold isostatic pressing were also applied to fabricate Bi-2223 bulks [15]. Bars with 17.8 cm in length were made by uniaxially pressing Bi-2223 powder having (1.7/0.34)223 and (1.8/0.4)223 phase composition. The bulk bars were densified by subjecting them to a schedule of alternate liquid-phase sintering and cold isostatic pressing. Critical current densities approximately equal to 1000 A/cm² (critical currents of 750 A at 77 K in self-field conditions) were achieved.
Sinter forging has been proven more effective than the other techniques in improving the critical current density for bulk high Tc ceramics [16]. Bulk Bi-2212 bars were fabricated by directional solidification and bulk Bi-2223 bars by cold isostatic pressing and sintering or by sinter forging. Maximum transport $J_c$ values at 77 K were 450 A/cm$^2$ for the Bi-2212, 1000 A/cm$^2$ for the pressed and sintered Bi-2223 bar, and 8000 A/cm$^2$ for the sinter-forged Bi-2223 bar. The Bi-2212 bar exhibited the lowest strength and fracture toughness, and the sinter-forged Bi-2223 bar the highest strength and toughness.

High critical current densities of nearly $10^4$ A/cm$^2$ at 77 K have been reported for Bi-2223 bulks by several groups [17, 18, 19]. A transport critical current density of 6900 A/cm$^2$ at 77 K in self-field was reported for Bi-2223 small bulk sample by Rouessac et al. [17]. Dense Bi(Pb)-2223 superconductor with highly oriented structure were prepared by sinter-forging at a temperature between 840 °C and 850 °C in air under a load of up to 30 MPa. Bi-2223 phase partially decomposed when the load was high, but an optimized stress profile minimized the decomposition or aided the recovery of the Bi-2223 phase. A remarkable improvement in critical current density ($J_c$ greater than $10^4$ A/cm$^2$) was reported by Tampieri et al. using a multi-step process with sinter forging [18,19]. Bulk BSCCO (2223) was prepared by a multi-step process (high cold pressing + pressureless sintering + hot-forging), and the final density of the samples exceeded 95% of the theoretical density, while the orientation factor increased up to 86%.
The effect of sinter forging on the field dependence of the critical current density was reported by different research groups [20, 21]. Advances in the densification process lead first to an improvement in the electrical connectivity between grains (transport $J_c$ increases) and then to a deterioration of both intragranular and intergranular properties ($T_c$, magnetic $J_c$ and transport $J_c$ decrease) because of the induced loss of oxygen, a continuous 2212 intergrain network, and other defect formation [20]. Dou et al [21] compared magnetic properties of Bi-Pb-Sr-Ca-Cu-O superconductors, fabricated by various techniques: “normal sintering”, “powder-in-tube”, “hot-pressing” and “hot isostatic pressing”. For Ag-sheathed tapes and hot-pressed samples, the $J_c$ dropped 80% when the magnetic field was increased from the ambient earth field to 0.5 T, whereas that of the normally sintered samples decreased by two orders in a magnetic field of only 0.01 T.

Several factors having an influence on critical current density have been reported [22, 23]. The powder starting stoichiometry has an effect on the critical current density [22]. BSCCO (2223) superconducting powders were prepared by three different techniques (solid state, pyrolysis and sol-gel) and with three different stoichiometries, essentially based on variations of the Ca/Sr ratio and the Cu concentration. Different hot-forging cycles were then applied to attain a greater density and orientation factor. It was found that the process phenomenology was strictly linked to the powder starting stoichiometry: when the composition was very near to the theoretical (2223), the effects of secondary phase extrusion were observed during hot forging, yielding a purification and inhibition of (2212) formation accompanied by an appreciable increase in $J_c$ with respect to the hot-pressed samples. On the other hand, when the Ca/Sr ratio was considerably greater than
one and the Cu excess was low, recrystallization of Bi-2223 phase from the liquid took place, with a remarkable improvement in the critical current density ($J_c$ greater than $10^4$ A/cm$^2$) [22]. To promote densification, the multi-step synthesis and hot pressing at 855 °C for 50 hours was found to be adequate to produce a high-purity (2223) phase and strong textures [23].

Effects of preliminary annealing and intermediate grinding on the properties of hot pressed bars were investigated by Pachla et al [24]. Optimal structural and physical properties were obtained for preliminary annealing of 100–120 h duration and subsequent hot pressing under a pressure of about 25 MPa for 80 h at 850 °C. Dense 2223 single-phase bulk bars of ~ 0.3 mm$^2$ cross-section were fabricated by uniaxial hot pressing [24].

The advantage of the sinter forging method is that the material is uniaxially pressed at a high temperature that is close to the melting temperature of this material. It is thus an effective method for significantly improving the texture of Bi-2223 material and results in a $J_c$ improvement. The best $J_c$ achieved by this method is ~ $10^4$ A/cm$^2$ at 77 K [18-20]. However, sinter forging has not been employed to fabricate large bulk samples by other groups working on high-$T_c$ superconductors. Even so, there is no evidence to show that this technique should only be restricted to small sample fabrication. Cold uniaxial pressing has been used to make green compacted pellets. However, it is of limited use for producing large samples with complicate shapes. Cold isostatic pressing (CIP) can solve this problem.
The influence of the sinter forging deformation rate on critical current density behavior in external fields for Bi-2223 bulk samples is investigated in this chapter. The bulk samples were fabricated by two methods, each with three steps: (1) cold isostatic pressing (CIP), pre-sintering and sinter-forging, or (2) pre-sintering, cold isostatic pressing (CIP) and sinter forging. The results revealed that the \( J_c \) is strongly affected by the deformation rate of the sinter forging for both cases. The \( J_c \) of samples processed by method 1 is also much higher than that of samples processed by method 2. From measurements of the field dependence of the critical current density, it was revealed that sinter forging can improve critical current density behavior in external fields, particularly below 50 mT. The correlation of pinning force and deformation rate is also investigated.

4.2 Two processing procedures

Two batches of samples having a cation ratio of Bi/Pb/Sr/Ca/Cu = 1.72/0.34/1.83/1.97/3.13 were prepared by two schedules, as shown in Fig. 4.1. One started with cold isostatic pressing (CIP), shown in Fig. 4.1 (a); another method began with sintering in air, shown in Fig. 4.1 (b). Processing procedures included pre-sintering, cutting into pellets and sinter forging, but CIP was the first step, and sintering in air was the second step for the first batch of samples. The contacts used for measurement were inserted in between two isostatically pressed samples. The pressure applied during the sinter forging varied from 0.3 MPa to 7 MPa, and the total time of sinter forging was 50 hours. The final dimensions of the samples were \( \sim 0.3 \times 0.8 \times 2 \) cm\(^3\). Field dependence of the transport critical current density \( J_c \)- H was obtained using a four-probe method with a 1
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$\mu$V/cm criterion with the direction of the external field parallel and perpendicular to the broad surface of the samples.

4.3 Critical current density of Bi-2223 bulk samples made by two procedures (at 77 K, self-field)

Fig. 4.2 shows a photo of a bulk sample prepared by a combination of CIP and HP. The sample has a bridge cut after hot pressing shown between the two inner contacts. The sample number, deformation rate, original critical current ($I_c$) and critical current density ($J_c$), and the dimensions of each bridge for selected samples, as well as the $I_c$ and the $J_c$ for a sample with a bridge in self-field at 77 K are shown in Table 4.1.
Chapter 4: Effect of pre-sintering and deformation rate

Fig. 4.1 Schematic diagram of two processing methods with pre-sintering conducted (a) after CIP and (b) before CIP.
Chapter 4: Effect of pre-sintering and deformation rate

Fig. 4.2. A photo of a bulk sample with a bridge cut after sinter forging.

In Table 4.1, all samples are labeled with Fc, which means samples started with CIP processing. In the same way, Fs means samples started with sintering (Table 4.2). Fc0, Fc1, Fc2, Fc3, Fc4 and Fc5 refer to samples with different deformation rates: 0%, 30%, 60%, 70%, 80% and 90%. Fs0, Fs1, Fs2, Fs3 and Fs4 have deformation rates of 0%, 50%, 70%, 80% and 90%. The final number on the code is used to describe samples with the same deformation rate, i.e, Fc0.1, Fc0.2 and Fc0.3 are the samples having the same deformation rate of 0%.
It is seen that \( J_c \) for both batches of samples, was strongly dependent on the deformation rate of the sinter forging. For the first batch of samples beginning with CIP, the \( J_c \) increased from 115 A/cm\(^2\) to 778 A/cm\(^2\) as the thickness reduction rate increased from 30\% to 80\%, respectively, but it decreased as low as 146 A/cm\(^2\) as the thickness reduction rate was further increased to 90\%. This is because too much sinter forging causes cracks, resulting in a decrease in \( J_c \). For the second batch of samples beginning with pre-sintering, the \( J_c \) varied with deformation rate, but the maximum critical current density achieved was 432 A/cm\(^2\), much lower than 778 A/cm\(^2\) achieved by the first processing procedure. So, the first method (CIP conducted before pre-sintering, followed by sinter forging) demonstrated better result than the second method.

\( J_c \) measurements were further carried out for some samples on which a bridge was prepared, as shown in column 7, Table 4.1 and Table 4.2. Four samples were chosen from the first batch of samples with deformation rates of 30\%, 70\% and 80\% and one from the second batch with a deformation rate of 70\%. The critical current density was higher for all four samples after the bridges were cut, as shown in Table 4.1 and Table 4.2. The biggest increase in \( J_c \) was from 778 A/cm\(^2\) to 1970 A/cm\(^2\) for sample Fc4.1 which started with CIP and a deformation rate of 80\%, and the \( J_c \) of sample Fs2.2 that started with pre-sintering was also almost doubled from 374 A/cm\(^2\) to 694 A/cm\(^2\).
Table 4.1 Some parameters and properties for samples processed by method 1.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Thickness reduction rate (%)</th>
<th>Pressure applied (MPa)</th>
<th>Dimensions (cm$^3$) (Thickness×Length ×Width)</th>
<th>$I_c$ (A)</th>
<th>$J_c$ (A/cm$^2$)</th>
<th>Dimensions (cm$^3$) (Thickness×Length×Width) (Bridge)</th>
<th>Critical current (A)</th>
<th>Critical current density $J_c$ (A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fc0.1</td>
<td>0</td>
<td>0</td>
<td>0.29×0.65×1.8</td>
<td>18.6</td>
<td>98</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fc0.2</td>
<td>0</td>
<td>0</td>
<td>0.3×0.65×1.7</td>
<td>19.6</td>
<td>101</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fc0.3</td>
<td>0</td>
<td>0</td>
<td>0.28×0.6×1.7</td>
<td>17.8</td>
<td>105</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fc1.1</td>
<td>30</td>
<td>1.1</td>
<td>0.35×0.76×1.9</td>
<td>37</td>
<td>139</td>
<td>0.35×0.24×0.25</td>
<td>16.6</td>
<td>182</td>
</tr>
<tr>
<td>Fc1.2</td>
<td>30</td>
<td>1.1</td>
<td>0.35×0.75×1.85</td>
<td>30.3</td>
<td>115</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fc2.1</td>
<td>60</td>
<td>3.5</td>
<td>0.3×0.78×2.6</td>
<td>72</td>
<td>308</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fc2.2</td>
<td>60</td>
<td>3.5</td>
<td>0.2×0.85×1.65</td>
<td>69.5</td>
<td>400</td>
<td></td>
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<tr>
<td>Fc3.1</td>
<td>70</td>
<td>4.5</td>
<td>0.22×0.8×1.15</td>
<td>93.4</td>
<td>531</td>
<td></td>
<td></td>
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<tr>
<td>Fc3.2</td>
<td>70</td>
<td>4.5</td>
<td>0.2×0.55×2.1</td>
<td>58.5</td>
<td>532</td>
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<tr>
<td>Fc3.3</td>
<td>70</td>
<td>4.5</td>
<td>0.2×0.55×1.9</td>
<td>53.2</td>
<td>484</td>
<td>0.2×0.28×0.25</td>
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<tr>
<td>Fc4.1</td>
<td>80</td>
<td>5.2</td>
<td>0.3×0.75×2.9</td>
<td>175</td>
<td>778</td>
<td>0.3×0.95×0.25</td>
<td>56.3</td>
<td>1970</td>
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<tr>
<td>Fc4.2</td>
<td>80</td>
<td>5.2</td>
<td>0.23×0.75×1.75</td>
<td>87.1</td>
<td>672</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Fc5.1</td>
<td>90</td>
<td>6.8</td>
<td>0.3×0.8×2.3</td>
<td>34.5</td>
<td>146</td>
<td>0.3×0.34×0.25</td>
<td>22.7</td>
<td>202</td>
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<tr>
<td>Fc5.2</td>
<td>90</td>
<td>6.8</td>
<td>0.3×0.78×2.6</td>
<td>72</td>
<td>308</td>
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Table 4.2 Some parameters and properties for samples processed by method 2.

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<th>Sample No.</th>
<th>Thickness reduction rate (%)</th>
<th>Pressure applied (MPa)</th>
<th>Dimensions (cm³) (Thickness×Length×Width)</th>
<th>Critical current density Jc (A/cm²)</th>
<th>Dimensions (cm³) (Thickness×Length×Width) (Bridge)</th>
<th>Critical current (A)</th>
<th>Critical current density Jc (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fs0.1</td>
<td>0</td>
<td>0</td>
<td>0.35×1.2×2.5</td>
<td>21</td>
<td>50</td>
<td></td>
<td></td>
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<tr>
<td>Fs0.2</td>
<td>0</td>
<td>0</td>
<td>0.37×1.2×2.5</td>
<td>23.5</td>
<td>53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fs1.1</td>
<td>50</td>
<td>2.8</td>
<td>0.31×1.2×2.5</td>
<td>63</td>
<td>169</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fs1.2</td>
<td>50</td>
<td>2.8</td>
<td>0.32×1.1×2.2</td>
<td>67</td>
<td>190</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fs2.1</td>
<td>70</td>
<td>4.2</td>
<td>0.25×1.1×2.2</td>
<td>104</td>
<td>378</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fs2.2</td>
<td>70</td>
<td>4.2</td>
<td>0.3×1.15×2.4</td>
<td>129</td>
<td>374</td>
<td></td>
<td>0.3×0.15×0.25</td>
</tr>
<tr>
<td>Fs2.3</td>
<td>70</td>
<td>4.2</td>
<td>0.3×0.9×2.1</td>
<td>87</td>
<td>322</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fs3.1</td>
<td>80</td>
<td>4.8</td>
<td>0.27×1.3×2.5</td>
<td>140</td>
<td>398</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fs3.2</td>
<td>80</td>
<td>4.8</td>
<td>0.28×1.2×2.5</td>
<td>145</td>
<td>432</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fs4.1</td>
<td>90</td>
<td>5.3</td>
<td>0.28×1.2×2.5</td>
<td>48</td>
<td>171</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fs4.2</td>
<td>90</td>
<td>5.3</td>
<td>0.27×1.05×2.2</td>
<td>46</td>
<td>162</td>
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</tbody>
</table>
4.4 Critical current density behavior in external fields (at 77 K)

Fig. 4.3 (a) shows the normalized $J_c$ vs external field at 77K for three samples started with CIP and deformed at a reduction rate of 0 %, (sample Fc0.3), 30 % (sample Fc1.1) and 80 % (sample Fc4.1). Fig. 4.3 (b) shows the normalized $J_c$ vs external field at 77 K for two samples with CIP (Fc3.3) or pre-sintering (Fs2.2) and deformed at a reduction rate of 70 %. From Fig. 4.3 (a), for the three samples, increasing the sinter-forging rate can enhance critical current density $J_c$ in an external field, in the particularly at low field region below 50 mT. The critical current density of sample Fc1.1 with a deformation rate of 30 %, decreased very quickly in the field region below 40 mT, remained almost the same in the region from 40 mT to 200 mT, and had the same trend as other samples (sample Fc3.3 and Fc4.1) above 200 mT, for both field directions (parallel and perpendicular to the sample surface). However, sample Fc4.1 performed differently in an external field, with critical current density decreasing much more slowly up to 1000 mT for both directions, particularly in the region below 50 mT. This indicated that sinter forging could somehow improve weak links or grain coupling between grains.

In Fig 4.3 (b), it is seen that the critical current density of sample Fs2.2, which had the same deformation rate as sample Fc3.3, decreased similarly to sample Fc3.3 in the low field region below 40 mT, but decreased much more quickly above 40 mT.
Fig. 4.3 (a) Normalized $J_c$ Vs external field at 77 K for three samples started with CIP and deformed at reduction rate of 0% (Fc0.3), 30 % (Fc1.1) and 80% (Fc4.1).
Fig. 4.3 (b) Normalized $J_c$ Vs external field at 77 K for two samples started with CIP (Fc3.1) or pre-sintering (Fs2.2) deformed at a reduction rate of 70%.
4.5 Normalized pinning force density for samples made by two procedures

In order to further clarify the different behaviors for samples made by the two procedures, the normalized pinning force density vs external field was calculated from the $J_c-H$ curve, i.e., $J_c H / (J_c H \text{max})$ or $F_p / F_p \text{max}$, represented in Fig. 4.4 and Fig. 4.5. Fig. 4.4 shows the normalized pinning force density against magnetic field for four samples (Fc1.1, Fc3.3, Fc4.1 and Fs2.2) at $H_{\text{c-axis}}$ and 77 K. It can be seen that the peak position of the pinning force density shifted from 200 mT to 500 mT as the deformation rate increased from 30% to 80% for the three samples, Fc1.1, Fc3.3 and Fc4.1, all started with CIP. This indicates that sinter forging could enhance the pinning force density when the external field is parallel to sample surface. However, for sample Fs2.2, the position of pinning force peak shifted to as low as 30 mT, ten times lower than sample Fc3.3 whose peak position was located at 300 mT. Both samples were deformed at the same reduction rate of 70%. The only difference between Fs2.2 and Fc3.3 was that the processing of Fs2.2 started with pre-sintering and Fc3.3 started with CIP.

Fig. 4.5 shows the normalized pinning force density against magnetic field for four samples (Fc1.1, Fc3.3, Fc4.1, and Fs2.2) at $H_{/c}$ and 77 K. It can be seen that the peak position of the pinning force density decreased with an increasing deformation rate from 30% to 80%, i.e. $F_p / F_p \text{max}(\text{Fc1.1}) > F_p / F_p \text{max}(\text{Fc3.3}) > F_p / F_p \text{max}(\text{Fc4.1})$. For three samples, Fc1.1 (reduction rate 30%), Fc3.3 (reduction rate 70%) and Fc4.1 (reduction rate 80%),
Fig. 4.4 Normalized pinning force vs external field for four samples at $H_{\parallel \text{C}}$.

The peaks of the pinning force density were lower than for sample Fc3.3 which had the same deformation rate of 70%. So, for the samples with CIP first, a higher deformation rate of sinter-forging can improve the flux pinning force density when the external field is parallel to sample surface, but degrades the pinning force when the external field is perpendicular to the sample surface. The sample with pre-sintering first has a 10 times lower pinning force density peak at the same deformation rate of 70% for both directions. However, the critical current density $J_c$ of both samples behaved similarly in external fields in the low field region below 40 mT.
4.6 XRD and micro structural features

Figure 4.6 (a) and (b) show the XRD diffraction patterns of samples at different stages of processing using two routes: pre-sintering conducted after cold isostatic pressing (a) and pre-sintering conducted before cold isostatic pressing (b). All samples for XRD measurement were crushed from the bulks, and then ground into fine powders. In the case of pre-sintering conducted after CIP, the precursor powders were directly pressed into long bulk bars, then the bars with high mass density were sintered at 850 °C for 120 hours, then
the pellets cut from the bars were sinter-forged twice. However, for the case of pre-sintering before cold isostatic pressing, the precursor powders were pressed into discs at a pressure of 30 MPa. Sinter forging was first carried out, and the discs were crushed and ground into powders again. These powders were then pressed into long bulk bars using cold isostatic pressing and then sinter forged twice. For route 1, XRD pattern 1 in Fig. 4.6 (a) showed that the precursor powder mainly consisted of Bi-2223 phase and minor phases such as Bi2201 and Bi-2212. XRD patterns (3) and (4) in Fig. 4.6 (a) revealed that the bulk deformed at 80 % deformation rate had a stronger texture compared with the sample without deformation. XRD pattern (2) in Fig. 4.6 (a) showed that only a small fraction of Bi-2212 phase was present. For route 2, XRD pattern (1) in Fig. 4.6 (b) showed that the precursor powder mainly consisted of Bi-2223 phase. XRD patterns (2) and (3) in Fig. 4.6 (b) were very similar and contained mainly Bi-2223 phase for the sample after pre-sintering and after CIP + sinter forging at a reduction rate of 80 %. The difference between the two routes is that the XRD patterns for route 1 have narrower peaks after sinter forging than for route 2.

Fig. 4.7 (a), (b) and (c) show the SEM images for bulks processed by route 1 and deformed at 0%, 30% and 80 % reduction rates, and Fig. 4.7 (d) for a sample made by route 2 and deformed at a reduction rate of 80%. From Fig 4.7 (a), (b) and (c), it is clear seen that the grains of all three bulks have a plate-like shape. It should be noted that the degree of texture and the grain contacts for samples deformed at reduction rate of 30% as shown in Fig 4.7(b) are better than for the un-deformed sample shown in Fig.4.7 (a). The degree of texture and grain contacts for a sample deformed at reduction rate of 80% shown in Fig.4.7(c) are better than for sample Fc1.1 shown in Fig.4.7 (b). This indicates that the
bulks sinter forged at higher deformation rates had better grain alignment and better grain contacts. This is why a sample deformed at a higher reduction rate has a higher critical current density. However, too high a deformation rate caused cracks, which appeared along the edges of the samples. These two factors make positive and negative contributions to critical current density. The bulks deformed at a reduction rate of 80% have a better compromise between these two factors and a higher critical current density. Fig. 4.7 (d) shows clearly that sample Fs3.2 (processed by route 2 and deformed at a reduction rate of 80%) has very small grains in the matrix and most grains have round ball shapes. The grain connectivity in this sample are not good as in the samples prepared by route 1. This is the main reason why the performance of bulks processed by route 2 is much poor than that of those samples processed by route 1.
Figure 4.6 (a) XRD patterns for (1) Bi-2223 precursor, (2) CIP pressed precursor after sintering at 850 °C/120 hours in air, (3) sample Fc0.1 with a reduction rate of 0%, and (4) Fc4.1 with a reduction rate of 80%.

Figure 4.6 (b) XRD serial patterns for (1) Bi-2223 precursor, (2) Normal cold pressed precursor after sintering 850 °C/120 hours in air, (3) sample Fs3.1.
Figure 4. SEM images for (a) sample Fc0.3 made by route 1 and un-deformed, (b) sample Fc1.1 made by route 1 and deformed at reduction rate of 30%.
Figure 4. 7 SEM images for (c) sample Fc3.2 made by route 1 and deformed at reduction rate of 80%, and (d) sample Fs3.2 made by route 2 and deformed at reduction rate of 80%.
4.7 Conclusions

A technique combining CIP and HP was applied to the fabrication of Bi-2223 bulks, and pre-sintering was conducted after (route 1) and before CIP (route 2). The effects of the deformation rate during sinter forging and pre-sintering were investigated. When pre-sintering was conducted after CIP (route 1), the critical current density of bulks at 77 K was much higher than for bulks made by route 2 (pre-sintering performed before CIP). Measurement of the field dependence of critical current density revealed that optimized sinter forging could improve the critical current density $J_c$ behavior in external fields, particularly in the low field region below 50 mT, for the samples where CIP was conducted before pre-sintering. For the samples initially pressed with CIP, a higher sinter-forging deformation rate can improve the flux pinning force when the external field is parallel to the sample surface, but degrades the pinning force density when the external fields is perpendicular to the sample surface ($H//c$, 77 K); a sample that was initially pre-sintered and deformed at a reduction rate of 70% has a pinning force peak position 10 times lower than that of the samples started with CIP and deformed at a reduction rate of 70% for both field directions ($H\perp c$ and $H//c$, at 77K). However, when a sample was started with pre-sintering and deformed at a reduction rate of 80%, the critical current density $J_c$ behaved similarly in external field to a sample started with CIP in low field region below 40 mT (77K), but $J_c$ decreased much more quickly at fields over 40 mT.
References


Chapter 5: Properties of prototype Bi-2223 bulk current lead

5.1 Introduction

To apply a high- $T_c$ superconductor in current leads, improvements in contact resistance ($R_c$) and in critical current density ($J_c$) are both equally important [1]. Contact resistance is an important parameter for a number of practical applications of current leads. Several techniques have been developed to fabricate contacts for different requirements [3, 4, 5]. The contact resistivity is normally of the order $10^4$ to $10^5 \ \Omega \ cm^2$ for bulks prepared by soldering, but there is always a problem with mechanical stability. E. Lorenz et al. made soldered contacts to ceramic YBa$_2$Cu$_3$O$_7$ samples. A relatively thick and adherent layer of the contact metal Ag or Cu was laid down on the surface of the superconducting sample. Onto this metal layer, contact wires were soldered by a standard soldering process. Without further heat treatment, contact resistance values of the order of $10^{-4} \ \Omega \ cm^2$ were obtained. By additional annealing, the contact resistance could lowered to values below $10^{-6} \ \Omega \ cm^2$ [2].

The contact resistance was improved up to a range of $10^{-6}$ to $10^{-7}$ by using a technique of sintering silver film deposited on high-$T_c$ ceramics [3]. The surface contact resistivities of high $T_c$ superconductors with different methods of connection were compared. The current - voltage (I - V) characteristics of the contacts were investigated and analyzed. It was found that the amount of silver added to an YBCO superconductor affected the contact resistance between the lead and sample. The lowest surface contact resistivity, $1.3 \times 10^{-7} \ \Omega \ cm^2$, was obtained using a method involving sintering of a silver film.
The contact resistance of several metals (Au, Ag, Cu, Pb, Sb and Al) deposited on YBa$_2$Cu$_3$O$_{7-x}$ has been investigated by Oka at al. who concluded that Ag and Au are the most suitable candidates to be used as contact terminal metals [4]. Contacts with several metals, Ag, Au and Cu, on YBa$_2$Cu$_3$O$_{7-x}$ have lower resistivity. They have different tendencies for oxidation. It is suggested that the main sources of contact resistance are the formation of an oxide layer on the metal side of the interface and the occurrence of an oxygen-deficient layer on the YBCO surface. By using Au, Ag and Cu, for which free energy are high, electrodes of good quality were obtained where the contact resistivity was less than $10^{-6}$ Ω cm$^2$.

Bi-2223 is more stable than YBCO against degradation due to contact resistance. Grajcar et al. studied the time evolution of point contact resistances for two high-T$_c$ superconductors, YBa$_2$Cu$_3$O$_x$ and Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$ [5]. The resistance of YBa$_2$Cu$_3$O$_x$/In, Au and Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$/In, Ag point contacts were observed for different period of time. The results are discussed in terms of work oxygen diffusion from the surface layer of high-T$_c$ superconductors. From a comparison of the two materials it is clearly seen that the surface of BSCCO is more stable than YBCO; nevertheless, the surface degradation processes due to oxygen diffusion are significant for both materials within the room temperature range. The sharp drop in the time increase of the point contact resistance at temperature ($T_s$), which approximately equals 220 K for YBCO and approximately equals 185 K for BSCCO, is interpreted as due to oxygen reordering in the unit cells of high-T$_c$ superconductors [5].
Research results revealed that the contact resistance was improved by Ag addition [6]. The effect of Ag addition on Bi-2223 bulks fabricated by the cold isostatic pressing and sintering process was studied. Addition of 5 wt.% Ag resulted in an increase in $J_c$ values from 500 to 800 A/cm² and in a decrease in $R_c$ values from $10^{-6}$ to $10^{-7}$ Ω cm² at 77K, 0T. These improvements were due to both an increase in the size of the Bi-2223 grains and an increase in density of the sintered bulk. The results indicate that Ag addition did not affect the thermal conductivity since the Ag particles dispersed homogeneously in the sintered Bi-2223 bulk.

Because they are subjected to Lorentz force or forces due to differential thermal contractions of the sample holder, these forces may cause significant mechanical damage to current leads. In melt-textured growth (MTG) samples the contact resistivity in the contacts can be very high and dissipation may cause heating which can lead to faulty measurements or even to thermal runaway [7]. The losses are determined by the resistance of the normal metal, the contact resistance and the transfer length in the Y-Ba-Cu-O. Even when very low resistance contacts are realized, the sample still often breaks under the Lorentz force or forces due to differential thermal contractions of the sample holder. To avoid this problem, Grajcar et al. developed a new sample holder which reinforces the sample and optimizes the geometry of the normal conducting part to achieve good heat exchange with the cryogenic liquid and to reduce the Joule heating. In their report, they discuss the influence of the sample holder on thermal stability and present the $J_c$ values at various temperatures and fields [7].
For Bi-based bulks, weak links between grains are the major obstacle to further improving critical current density. In a study of intergranular and intragranular currents in Bi-2223 bulks [8,9], the temperature dependence of intragranular currents exhibited a typical behavior for S-N-S (superconductor-normal metal-superconductor) junctions. For intergranular currents the temperature dependence suggested a limitation due to thermally activated flux creep in the space between the superconducting grains. The intergranular current is obviously related to the transport current, which is an essential issue from the point of view of practical application. Up to now, many attempts have been made to improve the transport critical current density for Bi-based bulk superconductors.

Several techniques have been developed to fabricate Bi-based bulk superconductors. Yamada et al used the diffusion reaction process to fabricate Bi-2212 oxide cylinders with large transport $I_c$ and $J_c$ as well as low contact resistance [10]. The substrate with a Sr:Ca:Cu atomic ratio of 2:1:2 was pressed into a cylindrical rod by cold isostatic pressing, and then sintered. The heat treatment was performed to produce the Bi-2212 diffusion layer. The Bi-2212 diffusion phase, formed at the coating layer with Bi:Cu ratio of 2:1 and Ag$_2$O addition was coated around the surface of the substrate. The transport $J_c$ decreased with temperature, being about $10^4$ A/cm$^2$ at 35 K at 0.5 T. The melt cast process (MCP) technique was also used to improve the properties of Bi-2212 [11,12]. The laying on low resistance contacts was integrated into the fabrication process. Critical current densities of 2.5-4 kA/cm$^2$ were obtained in self-field, with about 1kA/cm$^2$ measured for the full rods. It should be noted, however, that these were small samples.
Significant effect has been focused on enhancing $J_c$ of Bi-2223 superconductors. Bi-2223 bars with a $J_c$ of $\sim 10^3$ A/cm$^2$ were achieved using liquid-phase sintering and cold isostatic pressing [13]. Liquid-phase sintering temperatures were optimized from differential thermal analysis and study of the microstructure morphology. Low-resistance silver contacts were applied to the bars by hot-pressing at 820 °C and 3 MPa.

A high critical current density of $10^4$ A/cm$^2$ was achieved on Bi-2223 bulks of small size by using sinter-forging techniques [14-17]. Tampieri et al prepared the BSCCO (2223) bulks [14, 15, 16] with Bi-2223 superconducting powders prepared by three different techniques (solid state reaction, pyrolysis and sol-gel) and with three different stoichiometries, based on variations of the Ca/Sr ratio and the Cu concentration. When the Ca/Sr ratio is considerably greater than 1, recrystallisation of Bi-2223 phase from the liquid takes place, with a remarkable improvement in critical current density ($J_c$ greater than $10^4$ A/cm$^2$).

Murayama et al. also obtained a critical current density of $\sim 10^4$ A/cm$^2$ in Bi-2223 small bulks. It was concluded that one of the reasons for the increase in $J_c$ in the sample was the disappearance of a Bi,Pb-rich phase, probably the 2212 phase, as observed in scanning transmission electron microscopy [17]. Bulk $\text{Bi}_{1.80}\text{Pb}_{0.34}\text{Sr}_{1.87}\text{Ca}_{2.02}\text{Cu}_{3.0}\text{O}_y$ superconductors with a relative density of about 90% were prepared by hot pressing. The cold pressed sample was then hot-forged at 840 °C and a
pressure of 9.8 MPa in air for 50 h, and was also heat-treated at 885 °C for 15 min. during hot forging.

Sinter-forging has thus been widely applied to fabricate small pellets, and critical current densities ~10^4 A/cm^2 have been achieved at 77 K [14, 17]. This method has the potential to be used for fabricating large size bulks for applications, such as current leads. On the other hand, cold isostatic pressing (CIP) is a suitable technique for preparing large size and complicated shaped samples for ceramic powders. In this work, the combination of CIP and sinter forging was used to fabricate Bi-2223 current leads, and their critical current density performances and contact resistances were investigated.

5. 2. Experimental

The samples were fabricated by a combination of CIP and sinter-forging methods. The rods with mainly Bi-2212 phase were prepared by CIP with the stoichiometric ratio Bi/Pb/Sr/Ca/Cu=1.72/0.34/1.83/1.97/3.13, then sintered at 850 °C for 120 hours in air. Pellets cut from the rods were sinter-forged twice at 850 °C for 25 hours, and their total thickness reduction rates varied from 0 to 90% by applying different pressures (from 0 MP to 7 MP) during the process. The four terminals to be used for measurements were prepared and inserted at the second sinter forging. The complete processing details have been reported earlier [18]. The final dimensions of the samples were around 0.3cm x 0.7cm x 5.5 cm. The field dependence of the transport critical current density Jc-H was measured by the four-probe method with a 1μV/cm criterion and with the external field applied both parallel and perpendicular to the broad surface of the
samples. The bulk density and contact resistance were measured by the Archimedes method and four probe method, respectively [described in Chapter 2].

Fig. 5.1 A photo of a sample after sinter forging (lower) and a prototype (upper) of a current lead.

5.3. Results and discussion

Fig. 5.1 is a photograph showing a sample after sinter forging and a prototype of a current lead. The prototype sample was enclosed in a stainless steel tube for protection.

5.3.1. Critical Current Density Performance

Table 5.1 lists the critical current densities for samples that have undergone different sinter-forging rates, 0%, 30%, 60%, 80% and 90%. The values of critical current and critical current density are the average of measurements on three samples. The results revealed that critical current density $J_c$ at 77 K initially increased with increasing
deformation rate, reached the highest value of 725 A/cm² at 80%, and then decreased with further increases in the deformation rate. This indicates that the optimization of the deformation rate could significantly enhance the critical current density. After post annealing the highest $J_c$ exceeded 1000 A/cm² at 77 K and zero external field [18].

Table 5.1. Sample parameters and their properties (77 K).

<table>
<thead>
<tr>
<th>Batch No.</th>
<th>Thickness reduction rate (%)</th>
<th>Critical current $I_c$ (A)</th>
<th>Critical current density $J_c$ (A/cm²)</th>
<th>Mass Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>18.7</td>
<td>101</td>
<td>3.8</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>33.7</td>
<td>127</td>
<td>4.2</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>70.8</td>
<td>309</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>131</td>
<td>725</td>
<td>5.2</td>
</tr>
<tr>
<td>5</td>
<td>90</td>
<td>53</td>
<td>227</td>
<td>5.3</td>
</tr>
</tbody>
</table>

The $J_c$-$H$ measurements revealed that a proper deformation rate could also improve the critical current density performance in an external field at 77 K. In order to compare the influence of different deformation rates on critical current density behavior, the normalized field dependence of the critical current density is presented in Fig. 5.2 for three samples with deformation rates of 0%, 30% and 80%. For the sample with the 0% deformation rate, $J_c$-$H$ is not dependent on the direction of the external field because the grains of this sample have no preferred orientation, and the critical current decreases more quickly below 10 mT compared to the other two samples. On the other hand, there are two curves for the other two samples No. 2 and No. 4 with deformation rates of 30% and 80% respectively, for an external field parallel and perpendicular to the sample's broad surface as shown in Fig. 5.2. The critical current for the sample with a deformation rate of 80 % decreases much more slowly than for the other two samples.
in the region below 10 mT. However, in the region of external field higher than 110 mT, all three samples show the same behavior and all decrease rapidly with increasing field.

![Diagram](image)

Fig. 5.2 Normalized magnetic dependence of transport $J_c$ at 77 K for three samples with deformation rates of 0%, 30% and 80%, respectively.

5.3.2. Contact Resistance

Contact resistance $R_c$ measurements show that applied current for the samples with higher deformation rates becomes less dependent on transport current, as shown in Fig. 5.3 (a) and Fig. 5.3 (b). Fig. 5.3 (a) presents the contact resistance $R_c$ as a function of transport current. The results revealed that contact resistance $R_c$ increases with increasing transport current for all four samples, but it becomes much less dependent on transport current for higher deformation rates. For example, the sample with a
Fig. 5.3 (a) Contact resistance vs transport current at 77 K, measured by the four-probe method, (b) Ratio of contact resistance and applied transport current vs deformation rate, which calculated from Fig. 5.3 (a).
deformation rate of 90% shows almost no increase in $R_c$ as transport current increases from 0.5A to 50 A. The ratio of $R_c$ and the transport current is plotted in Fig. 5.3 (b), and decreases with increasing deformation rate and is nearly zero for the sample with deformation rate of 90 %.

5.3.3. Morphology and microstructural features

SEM images revealed that the samples with a higher deformation rate have better grain alignment and denser morphology, as shown in Fig. 5.4 (a), Fig. 5.4 (b) and Fig. 5.4 (c) for samples with deformation rates of 0%, 60% and 80%, respectively. Grain alignment and density are the important factors which strongly affect the critical current performance [19]. A large proportion of irregular grain shapes and grains in poor contact with each other appear in Fig. 5.4 (a). Fig. 5.4 (b) shows that the morphology becomes denser and some grains have preferred orientations, compared with Fig. 5.4 (a). However, Fig. 5.4 (c), which represents the sample with a deformation rate of 80%, shows that the grains in this case form a highly oriented layered structure with plate like crystals with better grain connectivity and that the morphology becomes denser, compared with both Fig. 5.4 (a) and Fig. 5.4 (b). This also supports the data on mass density presented in Table 5.1. The density normalized by the Bi-2223 theoretical value, 6.3 g/cm$^3$ as a function of the deformation rate is plotted in Fig. 5.5. It clearly indicates that the mass density rapidly increases with deformation rates up to 60%, and then increases much more slowly with further increases in deformation rate up to 90 %. On the other hand, too much deformation causes transverse cracks, which are harmful to critical current density performance. Some cracks are actually visible on the edges of the sample with a deformation rate of 90%. These positive and negative factors compete each other, but the sample with a
Chapter 5: Properties of Bi-2223 bulk current lead prototype

Fig. 5.4 (a) A SEM image of a fractured cross section of a sample with a deformation rate of 0%.

Fig. 5.4 (b) A SEM image of a fractured cross section of a sample with a deformation rate of 30%.
Fig. 5.4 (c) A SEM image of a fractured cross section of a sample with a deformation rate of 80%.

deformation rate of 80% has the best compromise of all these factors. This is the reason why the sample with the deformation rate of 80% has the best critical current density, as shown in Fig. 5.2.

Cross-sectional images show that samples with higher deformation rates have a better interface between the silver and the ceramics. Fig. 5.6 (a) and Fig. 5.6 (b) present
Fig. 5.5 Density normalized by the Bi-2223 theoretical value (6.3 g/cm$^3$) as a function of deformation rate.

typical cross-sectional images of samples with deformation rates of 0% and 80%, respectively. The white part and dark part are silver and superconducting ceramics, respectively, and the bar in the picture represents 40 microns. From the two images, it is clearly seen that the sample with a deformation rate of 80% has a better interface between the silver and ceramics. This is why the higher deformation rate yields lower contact resistances, as shown in Fig. 5.3 (a) and Fig. 5.3 (b).
Chapter 5: Properties of Bi-2223 bulk current lead prototype

5.4 Conclusions

The influence of the sinter-forging rate on critical current density behavior ($J_c$) in an external field and on contact resistance $R_c$ for Bi-2223 current leads has been investigated. The current leads were fabricated by a combination of Cold Isostatic
Pressing (CIP) and sinter-forging methods with the thickness reduction rate ranging from 0% to 90%. The two silver contacts with the sample were also prepared during the sinter-forging. The results revealed that $J_c$ was strongly affected by the rate of deformation rate during sinter-forging and reached a maximum of 725 A/cm$^2$ (1000 A/cm$^2$ after post annealing) at a deformation rate of 80%. From the measurements of external magnetic field dependence on $J_c$, it was determined that sinter forging could improve $J_c$ behavior in external fields, particularly in the regime below 50 mT. Measurements of contact resistance $R_c$ were conducted for different transport currents at 77 K. Results showed that the contact resistance for the samples with higher deformation rates became less dependent on the transport current over a range of 0.5 A to 50 A.
References


Chapter 6: The effect of post annealing on critical current density of (Bi, Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$ bulk current leads

6.1. Introduction

Many efforts have been made to fabricate Bi-2223 current leads, because of their potential to achieve high critical current density $J_c$ [1], and low thermal conductivity, as well as resistance to environmental degradation [2, 3]. In order to improve the texture and mass density of bulk Bi-2223 material, hot forging or sinter forging has been used by some researchers, improving $J_c$ to a level of $\sim 10^4$ A/cm$^2$ for small pellets [4, 5] and $\sim 10^3$ A/cm$^2$ for current leads [6]. Starting powders and the sintering schedule also affect critical current density $J_c$ significantly [1], because they influence microstructure and second phases, which determine the properties. Post annealing is also an important factor affecting critical current density. Some results have revealed that post annealing improves the flux pinning and critical current density for Bi-2223 and Bi-2212 tapes. A significant enhancement of $J_c$ in a magnetic field for Ag-sheathed Bi-Pb-Sr-Ca-Cu-O (BPSCCO) tapes has been achieved by post-annealing at reduced temperature after processing [7]. This post-annealing at reduced temperature introduced extra oxygen into the oxide superconductor. Weak links were eliminated and $J_c$ was increased in the post-annealed tapes by a factor of 1.5 to 3 at 0 T over the normally processed tapes without post-annealing. The introduced oxygen ions are responsible for the enhanced $J_c$ and may affect two-dimensionality in superconductivity for the BPSCCO system. The effect of post-annealing on superconducting properties and microstructures of Bi(2212)/Ag tapes was systematically investigated [8]. Bi(2212)/Ag tapes were fabricated by the melt-growth method at various cooling rates in air, followed by furnace cooling. Post-annealing at
810 °C was carried out for improving $T_c$ and $J_c$. The $T_c$ of the as-solidified tapes was approximately 80K, which increased to approximately 90K after post-annealing. The $J_c$ values of as-solidified tapes were not consistent even for tapes made under the same fabrication conditions. Post-annealing improved the $J_c$ of samples with poor $J_c$ and leads to more consistent values. However, a sample with high a $J_c (4.2K, 0T)$ of $6 \times 10^4$ A/cm$^2$ after solidification was barely improved by post-annealing. The effect of (Pb,Bi)$_2$Sr$_2$Ca$_2$CuO$_y$ (3221) phase formation during post-annealing has also been investigated [9]. It was found that the 3221 phase content increased with annealing time when the sample was fully reacted. (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ (2223) tapes were post-annealed at 780 °C up to 10 h, and the (Bi,Pb)$_2$Sr$_2$CaCu$_2$O$_8$ (2212) phase content remained almost constant. The critical current density and irreversibility field of the annealed tapes decreased monotonically with increasing 3221 phase content. Square-shaped 3221 particles were observed in both grains and grain boundaries situated on the ab-plane and were held to be responsible for the degradation of the critical current density and irreversibility field of the annealed tapes. The critical current density versus magnetic field results showed an enhancement of weak link behaviour induced by 3221 phase for the annealed tapes, which reduces the number of the strongly coupled grain boundaries.

Some researchers reported that the post annealing also has a significant effect on the critical current density of Bi-2212 bulks [10, 11]. The sinter-forging process for Bi-Sr-Ca-Cu-O (2212) superconducting ceramic, synthesized by a polymer matrix method has been optimized [10]. A maximum $J_c$ close to 700 A/cm$^2$ has been achieved under a pressure of 31.4 MPa and a temperature of 840 °C showing that annealing under O$_2$/N$_2$ also has to be optimized to obtain higher $J_c$ values in such sinter-forged bulk materials. Bi-2212 oxide superconductors were synthesized by the diffusion reaction
between a high melting point Sr-Ca-Cu oxide substrate and a low melting point Bi-Cu oxide coating layer [11]. Post-annealing in an inert gas atmosphere improved $T_c$ and $J_c$ at higher temperatures.

In this work, current leads were prepared by using a multi-step procedure, including cold isostatic pressing (CIP), pre-annealing, sinter forging (HP) and post-annealing. The effects of the deformation rate of sinter forging and post annealing on critical current density $J_c$ were studied.

6.2. Experimental procedures

$\text{Bi}_{1.72}\text{Pb}_{0.34}\text{Sr}_{1.83}\text{Ca}_{1.97}\text{Cu}_{3.13}\text{O}_x$ powders were prepared by spray pyrolysis of nitrate solution, then pressed into rods with a pressure of 400 MPa by using the CIP technique. The processing details are described elsewhere [6]. Short rods 5 cm long were sintered at 850 °C for 120 hours in air, followed by sinter forging 2 or 3 times at 850 °C for 24 hours and under a pressure range of 1~ 4 MPa. After each sinter forging, the rectangular samples were cut into two pieces of equal width along the longitudinal direction, and the two pieces were then overlaid for the next sinter forging. A post annealing was conducted at 825 °C for 24 hours in a 7.5 % $\text{O}_2$/N$_2$ flowing atmosphere, followed by furnace cooling. The annealing was repeated once under the same conditions. The transport critical current density $J_c$ was measured for each current lead with a 1 $\mu$V/cm criterion after sinter forging and after each post annealing. The phases and microstructure were studied by XRD and SEM.

6.3. Results and discussion

The final dimensions of the current leads after sinter forging were 5.5 cm in length, 0.2 ~ 0.4 cm in thickness and 0.56 ~ 0.85 cm in width. Table 6.1 lists three values of
critical current density $J_c$ for four samples having different thickness reduction rate, after sinter forging, after the first annealing and after the second annealing in 7.5 % $O_2$ / $N_2$ for 24 hours. Samples No.1, No. 2 and No. 3 were sinter forged twice, while sample No. 4 was sinter forged three times. The thickness reduction rates in Table 6.1 are calculated by using the formula $(t_0-t)/t_0$, where $t_0$ and $t$ are the thickness before and after sinter forging, respectively. It can be seen that the critical current density $J_c$ was improved from 193 to 325 A/cm$^2$, as the total thickness reduction rate increased from 51 % to 86 % even though all three samples were sinter forged twice. It should be noted that $J_c$ reached 910 A/cm$^2$ for the sample which was sinter forged three times and had a thickness reduction rate of 91 %. Meanwhile, Table 6.1 reveals that post annealing in 7.5 % $O_2/N_2$ improved the critical current densities for all four samples, which showed a 20 ~ 40 % increase. The critical current density $J_c$ reached 1050 A/cm$^2$ and 1100 A/cm$^2$ for sample No. 4 after the first and second post-annealing, respectively.

SEM observations revealed that sinter forging had improved the grain texturing and connectivity. For instance, the thickness reduction rates of sample No. 4 were 78 % and 96% after sinter forging 2 and 3 times, respectively. The higher deformation rate was associated with much better average grain alignment and grain connectivity. Fig. 6.1 (a), (b) and (c) show the SEM images of samples No.1, No.3 and No.4, respectively. From the three images, it is obvious that Fig. 6.1 (c) has better grain texture than Fig. 6.1 (b), and that Fig. 6.1 (b) better than Fig. 6.1 (a). Also, Fig. 6.1(c) has the best grain connectivity and density. This is the reason why sinter forging causes a significant improvement in critical current density.
Table 6.1. Transport critical current densities $J_c$ of the current leads hot-pressed with different thickness reduction rates (at 77 K and self-field)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Times of sinter forging</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Total thickness reduction rate (%)</td>
<td>51</td>
<td>78</td>
<td>86</td>
<td>91</td>
</tr>
<tr>
<td>$J_c$ after sinter forging (A/cm²)</td>
<td>193</td>
<td>214</td>
<td>325</td>
<td>910</td>
</tr>
<tr>
<td>$J_c$ after first annealing (A/cm²)</td>
<td>257</td>
<td>250</td>
<td>406</td>
<td>1050</td>
</tr>
<tr>
<td>$J_c$ after second annealing (A/cm²)</td>
<td>271</td>
<td>288</td>
<td>466</td>
<td>1100</td>
</tr>
</tbody>
</table>

Fig. 6.1 (a)
Chapter 6: The effect of post annealing on critical current density of (Bi, Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$ bulk

Fig. 6.1 (b)

Fig. 6.1 (c)

Fig. 6.1 SEM images of sample No.1 (a), sample No.3 (b) and Sample No.4. (c).
Chapter 6: The effect of post annealing on critical current density of (Bi, Pb)2Sr2Ca2Cu3Oy bulk

The Jc improvement for the samples due to post-annealing is mainly attributed to phase transformation. Fig. 6.2 shows XRD patterns of ground powders for sample No. 1 at four different stages: after annealing (a), two sinter forgings (b), first (c) and second post-annealing (d). The major phase after sinter forging was Bi-2223, plus some minor Bi-2212 and Bi-2201 phase. After the first post-annealing, the relative content of Bi-2223 content increased, while Bi-2212 and Bi-2201 significantly decreased. Other samples had similar XRD patterns.

Fig. 6.2 XRD patterns of sample No.1 after annealing at 850 °C for 120 hours in air (a), two sinter forgings (b), first post-annealing (c) and second post-annealing in 7.5 % O2/ N2 (d).
Fig. 6.3(a) and Fig. 6.3 (b) show a TEM image and electron diffraction pattern of sample No.4 after three sinter forgings. It is seen that colonies are strongly textured along one direction as shown in Fig. 6.3 (a). The contact boundaries between colonies mainly overlapped along the broad faces of the two adjacent colonies and so colonies are well contacted each other. Fig. 6.3 (b) indicates that grains are Bi-2223 phase and crystallized quite well. This shows that this fabrication method is effective for improving the texture and connectivity of grains.

6.4. Summary

The effect of the deformation rate during sinter forging and annealing in 7.5 % O$_2$/N$_2$ on $J_c$ of (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$ current leads has been investigated. Current leads were prepared by a combination of CIP (Cold Isostatic Pressing) and sinter forging techniques. The samples were prepared by sinter forging 2 or 3 times (cutting each sample into two longitudinal pieces and then overlaying the two pieces together for the next sinter forging). The samples were annealed in 7.5 % O$_2$/N$_2$ two times at 825 °C for 24 hours each. The maximum critical current density achieved by this technique exceeded 1000 A/cm$^2$ at 77 K and self-field. The results revealed that both the deformation rate during sinter forging and annealing in a low oxygen atmosphere had a significant effect on the critical current densities.
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Fig. 3 (a) TEM image and (b) Electron Diffraction Pattern of sample No. 4 with three separate sinter forging steps.
Chapter 6: The effect of post annealing on critical current density of (Bi, Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$ bulk

References


Chapter 7: Electromagnetic properties of Bi-2223 Bar Current Leads fabricated by a Combination of CIP and Sinter Forging

7.1. Introduction

High-T\textsubscript{c} current leads have attracted much attention, because the high-T\textsubscript{c} oxides have a low thermal conductivity at temperatures below their T\textsubscript{c}, which allows a reduction in the amount of cooling liquid. Many attempts have already been made to use high-T\textsubscript{c} oxide superconductors for current leads [2, 3]. J. Bock et al. reported Bi-2212 current leads fabricated by the Melt Casting Process (MCP) with a critical current density of 2,200 A/cm\textsuperscript{2} at 77 K [4]. V. Plechacek et al. reported Bi-2223 tube current leads fabricated by Cold Isostatic Pressing (CIP) with a critical current density of 1,000 A/cm\textsuperscript{2} at 77 K [5]. V. Rouessac applied the Uniaxial Sinter-Forging method to fabricate well textured Bi-2223 pellets with 10,000 A/cm\textsuperscript{2} [6]. Up to now, the best J\textsubscript{c} obtained for bulk tube current leads exceeds 1000A/cm\textsuperscript{2} at 77k and self-field, while the best J\textsubscript{c} for the rod current leads made by the CIP method is 570A/cm\textsuperscript{2} at 77K and self-field [1,5]. However, so far no paper has reported on the application of sinter forging to the fabrication of high-T\textsubscript{c} current leads.

As AC susceptibility is used as a main method to study the electro-magnetic properties in this chapter, a review of the literature on AC susceptibility applications for superconductors is presented. AC susceptibility has been widely applied to study properties of superconductors, such as critical temperature, intergrain weak links, doping effects and phase structures. AC susceptibility was used to measure the critical temperature in single or mixed superconductor compounds [7]. X-ray powder
diffraction patterns and AC susceptibility proved that the largest fraction of the sample was 110K phase and that the low $T_c$ phase in the material had a transition temperature below 77K. AC susceptibility data on other samples showed a single transition with an onset temperature of 108 K [8]. The higher-$T_c$ phase of the Bi-Sr-Ca-Cu oxide high-$T_c$ superconductor was stabilized by partially replacing Bi by Pb. On the basis of X-ray diffraction and EDX data, it was concluded that Pb substitution promotes the growth of (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+x}$ phase. The effect of F doping in the (Bi, Pb)-Sr-Ca-Cu-O system was investigated by both resistance and AC susceptibility measurements together. The results indicated that F doping promotes the formation of 2223 phase and increases the $T_c$ [9].

AC susceptibility measurements are very effective for studying the intergrain and intragrain properties for superconductors [18]. AC susceptibility measurements were carried out as a function of temperature, frequency and AC field amplitude on a rectangular bar shaped high-temperature superconductor with a nominal composition of Bi$_{1.84}$Pb$_{0.34}$Sr$_{1.91}$Ca$_{2.03}$Cu$_{3.6}$O$_{10}$ prepared by the liquid ammonium nitrate method. As the frequency (AC field amplitude) increases, the intra- and intergranular AC loss peaks move to higher (lower) temperature, which indicates that AC losses are due to both hysteretic bulk pinning losses and viscous (flux flow) losses. It was concluded the texturing of high-temperature superconducting ceramics leads to an improved intergranular coupling [11]. The influence of texturing on the magnetic susceptibility of Bi-2223 was also studied. This was demonstrated on the basis of AC susceptibility measurements obtained when texturing Bi-2223 polycrystals through combined
magnetic melt texturing and hot pressing (MMTHP) and Y-123 bulk samples obtained through combined magnetic melt texturing and zone melting (MMTZM).

Inter- and intragranular effects in microwave absorption of (Bi,Pb)2Sr2Ca2Cu3Oy were also reported [12]. Detailed low DC-field microwave absorption (LFMWA) and AC-susceptibility measurements were performed over a wide temperature range for high-quality bulk and fine powder samples of the (Bi,Pb)2Sr2Ca2Cu3Oy compound. The features observed in fine powders are quite different from those observed in bulk samples. This allows one to make a separation of intragranular from intergranular effects. It was found that the intragranular critical current density was on the order of $10^4$ A/cm². This is probably the intrinsic critical current density in the c-direction of the Bi-2223 compound.

It was claimed that an intragranular loss peak was clearly observed in a bismuth-based compound for the first time [13], which indicates that the intragranular contribution is strongly increased. Complex AC susceptibility measurements over a broad field range (1 Oe ~ 100 Oe) were made on Bi-Pb-Sr-Ca-Cu-O (Bi-2223 phase) bulk samples obtained by combined magnetic melt texturing and hot pressing. Improved intergranular coupling is obtained in the direction perpendicular to the applied stress and the magnetic field direction. An intragranular peak is also observed for the same direction.

It has been reported that AC susceptibility is very useful for studying phase transformation. AC susceptibility data of the crystals revealed a change of superconducting volume fraction with different initial Bi ratios [14]. Evaluation of the
phase composition of BPSCCO bulk samples was made by XRD and susceptibility analysis. Researchers presented a comparison of the phase purity analysis, using XRD and AC-susceptibility measurements, on a number of BPSCCO samples, containing different ratios of the Bi-2212 and Bi-2223 phase [15]. The differences observed in the results of both techniques were correlated with the growth mechanism of the Bi-2223 phase. The higher values for the percentage of the Bi-2223 phase observed in AC-susceptibility analysis, could be explained by the assumption that there is a specific distribution of the Bi-2212 and Bi-2223 phase during particle growth, resulting in shielding effects.

In this chapter, a novel method combining of CIP and sinter forging was applied to fabricate Bi-2223 current leads. The critical current density achieved by this method reached as high as 1000A/cm² at 77K and self-field. The phases and microstructure were analyzed by XRD and SEM. The texture and weak link behavior were studied by pole figures and AC susceptibility, respectively. The results showed that the matrix density, grain connectivity and texture were improved significantly by this method.

7.2 Experimental Procedure

Precursor powder with a nominal composition of Bi$_{1.72}$Pb$_{0.34}$ Sr$_{1.83}$ Ca$_{1.97}$Cu$_{3.13}$O$_{10}$ was prepared by spray pyrolysis of nitrate solutions. The powder was then pressed into rods with 80% theoretical density by the CIP method. Pellets were cut from the rods and sintered at 845°C for 80 hours, followed by a process of sinter forging at 845°C for 24 hours with a pressure of 5 MPa. A post-annealing was conducted for the samples at 825°C for 24 hours in a 7.5% O$_2$/balanced N$_2$ atmosphere, followed by a slow cooling
to 800°C and furnace cooling to room temperature. The transport critical current density was measured by the four-probe method with a 1μV/cm transition criterion. The microstructure of the samples was characterized by means of X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The surface texture of the samples was analyzed using pole figure measurements.

AC susceptibility measurements were carried out on a Model SR830 DSP lock-in amplifier and USA CTI-cryogenics. The dimensions of the samples used for AC susceptibility were 0.2 × 0.2 × 0.9cm³.

7.3. Results and discussion

7.3.1 Transport properties

Fig. 7.1 is a photo of the Bi-2223 bar current lead. The dimensions of this sample are 0.27 cm thick, 0.86 cm wide and 5.5 cm long. The I-V curve measured at 77 K and self-field is shown in Fig. 7.2. Current leads with various shapes and fabricated by different methods are compared in Table 7.1. It can be seen that a critical current (Ic) of 225 A and a critical current density (Jc) 1000A/cm² at 77K and self-field have been achieved by this combined CIP and sinter forging method. These values are much higher than in those samples prepared by the CIP method alone.

7.3.2 Microstructures

Fig. 7.3 shows typical XRD patterns for the surfaces of the samples before sinter forging, after sinter forging and after annealing in 7.5 % O₂ balanced with N₂. Fig. 7.3 (a) indicates that the sample mainly consisted of Bi-2223 phase after CIP and annealing at 845°C for 80 hours. No strong grain alignment was detected at this stage.
Fig. 7.1 Photo of a Bi-2223 current lead fabricated by a combination of CIP and sinter forging.

Table 7.1. Comparison of transport properties of for Bi-2223 current leads prepared by different techniques (at 77 K and self-field)

<table>
<thead>
<tr>
<th>Sample shape</th>
<th>Fabrication method</th>
<th>$I_c$(A)</th>
<th>$J_c$(A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube[1]</td>
<td>CIP and sintering</td>
<td>990</td>
<td>1240</td>
</tr>
<tr>
<td>Rod [6]</td>
<td>CIP and sintering</td>
<td>220</td>
<td>570</td>
</tr>
<tr>
<td>Rod (this work)</td>
<td>combination of CIP and sinter forging</td>
<td>225</td>
<td>1000</td>
</tr>
</tbody>
</table>

Fig. 7.3 (b) shows that the degree of grain alignment of the matrix was significantly enhanced after sinter forging, although a trace of Bi-2212 phase still existed in the
samples. Fig. 7.3 (c) is the XRD pattern for the sample after annealing in low oxygen pressure. It can be seen that the Bi-2212 phase was reduced and the grains continued to grow, as indicated by the sharp diffraction peaks.

Fig. 7.2 I-V curve for current lead fabricated by a combination of CIP and sinter forging
Fig. 7.3 Typical XRD patterns of current leads (a) before sinter forging; (b) after sinter forging; and (c) after annealing in 7.5 % O₂.

The SEM images of the current leads are presented in Fig. 7.4. As shown in Fig. 7.4 (a), no substantial grain alignment is observed in the CIP processed sample, although the matrix is quite dense. Some voids are still present in the grains. Fig. 7.4 (b) is the typical microstructure of the sample after sinter forging. It shows that both grain alignment and mass density were significantly improved compared to the CIP processed sample. However the texture is not as good as that found in Bi-2223 tapes fabricated by the PIT method. Some misalignment angles between grains are above
Chapter 7: Electromagnetic properties of Bi-2223 Bar Current Leads fabricated by

15°. Consequently, grain connectivity in this sample is worse than in Bi-2223 tapes. According to the railway-switch model, the small-angle c-axis tilt grain boundaries constitute strong connections and represent good paths for the super-current [16]. Due to the large average misalignment angle and the poor grain connectivity between grains, the critical current density of the current leads is lower than that of tape, which reaches ~10^4 A/cm^2 at 77k and self-field.

There was no substantial grain alignment for the bar current leads fabricated by a CIP and sintering procedure. This has been qualitatively shown using the XRD pattern in Fig. 7.3 (a) and the SEM image in Fig. 7.4 (a). To investigate the grain alignment of the hot-pressed samples quantitatively, the (0010) peak pole figure was measured on the sample surface and the results are shown in Fig. 7.5 (a). Fig. 7.5 (b) is the curve of intensity vs Ψ calculated from Fig. 7.5(a), where Ψ is the Bragg angle 2 Θ. The Ψ is the angle between x-ray beam and the broad surface direction of a bulk sample. As shown in Fig 7.5 (a), it varies from 0° to 90°. The average accumulative mis-alignment angles Ψ 50% and Ψ 90% are 9° and 32° respectively. These values indicated that the grains have a good alignment [7].
Chapter 7: Electromagnetic properties of Bi-2223 Bar Current Leads fabricated by

Fig. 7.4 Typical SEM images for Bi-2223 current leads (a) before sinter forging and (b) after sinter forging.
Chapter 7: Electromagnetic properties of Bi-2223 Bar Current Leads fabricated by

Fig. 7.5 (a) (0010) pole figure of Bi-2223 bar current lead fabricated by a combination of CIP and sinter forging and (b) average integrated intensity percentage vs Ψ(degree), Ψ(50% | Ave) = 9°, Ψ(90% | Ave) = 32°.
7.3.3 Electromagnetic properties

Fig. 7.6 presents the AC susceptibilities for two samples: one after CIP and the low oxygen pressure treatment (a), while the other is after sinter forging and low oxygen pressure treatment (b). The measurement were conducted with $f = 117$ Hz and zero DC external field. The intra-grain component is essentially insensitive to the change in the ac field amplitude $H_{ac}$, while the coupling component is affected significantly by a change in amplitude $H_{ac}$ as small as $10^{-4}$ mT [17]. As seen in Fig. 7.6(b), the real part $\chi'$ transition is quite sharp for such a poly crystalline sample at temperature 109K, and the imaginary part $\chi''$ appeared with only one peak in two different AC field amplitudes. Moreover the peak shifted to lower temperature as the AC field increased.

In Fig. 7.6 (a), however, the imaginary part $\chi''$ appeared with two peaks in different AC field amplitudes: the first one representing the intra-grain response and the second related to inter-grain coupling or second phase Bi2212. The second peak position was about 95 K at a low ac field amplitude of 0.307 Oe and only shifted to lower temperature near 85 K for higher a.c. fields, indicating that it wasn’t from the Bi2212 phase contribution. Therefore, the second peak was related to inter-grain coupling. This is in agreement with the results reported by other researchers [10]. This conclusion has been confirmed by the measurement of the third harmonic susceptibilities, which are shown in Fig. 7.7(a) and (b). Fig. 7.7 (b) indicated that the grain links are very strong. Fig.7.7 (a) makes it obvious that the first peak was the intra-grain component and the second was the grain weak-link contribution. Compared to the curve of $\chi'$ vs T in Fig. 7.6 (a) showed an additional transition step at lower temperature which reflects the flux penetration into the boundaries between the grains as the temperature increased. So, it can be concluded that the second sample shown in Fig. 7.6 (b) has a much better inter-
grain coupling than that shown in Fig. 7.6 (a). That is, the weak links were significantly reduced by the sinter forging process.

Fig. 7.6 AC susceptibility for Bi-2223 current leads (a) after CIP and low oxygen annealing and (b) after sinter forging and low oxygen annealing.
Fig. 7.7 Third harmonic susceptibility for measurement (a) after CIP and low oxygen pressure annealing and (b) after sinter forging and low oxygen annealing.
7.4. Summary

A new method using a combination of cold isostatic pressing (CIP) and sinter forging (HP) was applied to the fabrication of Bi-2223 bar current leads. The critical current density ($J_c$) achieved by this method reached as high as 1000 A/cm$^2$ at 77K in self-field. This value is much higher than the best $J_c$ reported for bar current leads, which is 570A/cm$^2$ achieved by the CIP technique [1]. The phases and microstructures were analyzed by XRD and SEM. The texture and weak link behavior were studied by pole figures and AC susceptibility, respectively. The results showed that the matrix density, grain connectivity and texture were improved significantly by this method.
References

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Chapter 8: Behaviour of Critical Current Density and Grain Misalignment of Hot-Pressed Bi-2223 Bar Current Leads

8.1. Introduction

Lawrence and Doniach [1] predicted a dimension crossover from 3D to 2D in layered superconductors under the condition that the coherence length $\xi_c$ is smaller than the distance between these layers. Later, Kes et al. [2] proposed that for the high-$T_c$ superconductor Bi$_2$Sr$_2$Ca$_x$Cu$_2$O$_y$ (Bi-2212): (1) in an external magnetic field, the magnetic field component $B_{\perp c}$ aligned along the CuO$_2$ planes should not influence the superconductivity, and (2) only the magnetic field component $B_{\parallel c}$ perpendicular to the planes causes dissipative behaviour from 3D to 2D if the temperature is below the crossover temperature $T_o$. This hypothesis has been confirmed in the behavior of Bi-2212 thin films by Raffy et al. [3].

Bi-2223 high-$T_c$ superconductor satisfies the condition that the coherence length $\xi_c$ perpendicular to the superconducting layers is smaller than the distance between these layers, so it should display 2D behavior below its crossover temperature $T_o$. So far, the 2D critical current density behavior of Bi-2223 compound at 77 K has been confirmed in Bi-2223/Ag tapes [4,5]. The effective grain misalignment angle, calculated from the critical current curves $I_c (B, \theta)$, has been commonly used for describing the degree of grain misalignment [4,5]; it is an intrinsic property for a particular material and determined by the thermal–mechanical processing scheme.
Sinter forging was found effective for improving grain alignment and thus achieving a high critical current density [6,7]. (Bi,Pb)\textsubscript{2}Sr\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{10} bulk samples were pressed isothermally at 850 °C under a constant pressure of 15 MPa for 1 hour. [6]. It was found that the mass density significantly increased. In addition to high mass density, the grain alignment within the samples was also improved which produced a significant improvement in the $J_c$. To achieve a high $J_c$, a sample requires sintering prior to a reasonably long hot-pressing. Caillard et al [7] studied the degree of grain disorientation for highly textured Bi-2212 bulks prepared by sinter forging. The optimisation of the sinter-forging process for Bi-Sr-Ca-Cu-O (2212) superconducting ceramic was investigated. The precursor powder was pressed under uniaxial stresses ranging between 15.9 and 46.8 MPa, and heated between 830 °C and 845 °C. Rather well textured samples showing less than 5.6° disorientation for 50% of the grains with respect to the ab plane were obtained. A maximum $J_c$ close to 700 A/cm\textsuperscript{2} was achieved with a pressure of 31.4 MPa and a temperature of 840 °C showing that annealing under O\textsubscript{2}/N\textsubscript{2} need to be optimized to obtain higher $J_c$ values in such sinter-forged bulk materials.

The degree of texture is one of the most important factors affecting the superconductivity of Bi-2223 superconductor, which include phases, matrix density, and defects. In this work, sinter forging is used in order to improve the texture of the bar current leads. The effective grain misalignment angle, $\varphi_{\text{eff}}$, is used to measure the degree of texture. The average grain misalignment angle, $\varphi_{\text{av}}$, is also measured by the pole figure method. Other features, such as phase and microstructure, are observed by X-ray diffraction (XRD) and scanning electron microscopy (SEM).
8.2 Experimental procedure

Precursor powder with a nominal composition of Bi$_{1.72}$Pb$_{0.34}$Sr$_{1.83}$Ca$_{1.97}$Cu$_{3.13}$O$_x$ was prepared by spray pyrolysis of nitrate solutions. The powder was then pressed into rods with ~80% theoretical density by the CIP method. Pellets were cut from the rods and sintered at 845 °C for 40 h, followed by HP at 845 °C for 24 h with a pressure of ~3 MPa. A post-annealing was carried out for the samples in a 7.5%O$_2$/N$_2$ atmosphere, at 825 °C for 24 h, followed by a slow cooling to 800 °C, and then furnace cooling to room temperature. The critical current $I_c$ was measured as a function of magnetic field for B//bar surface and B⊥ bar surface directions, i.e., $I_c$ (B // bar surface) and $I_c$ (B ⊥ bar surface) with a 1 μV/cm criterion. The magnetic field was always perpendicular to the current for all measurements. The average grain misalignment angle, $\varphi_{av}$, was measured after removing the top thin layer of the pellets by using the pole figure method. The microstructure of the samples was investigated by means of XRD and SEM.

8.3 Results and discussion

8.3.1 Critical Current Behavior and Effective Grain Misalignment Angle

Fig. 8.1 is a photo of the Bi-2223 bar current lead fabricated by the combination of CIP and sinter-forging procedures. The final dimension, $I_c$ and $J_c$ at 77 K and self-field are listed in Table 8.1. The dimensions of this sample are 0.4 cm thick, 1.0 cm wide, and 5.4 cm long, and its transverse cross-section is 0.4 cm$^2$. The critical current and critical current density are 119 A and 300 A/cm$^2$ at 77K and self-field, respectively. The I-H curve for different external magnetic fields, measured at 77K with fields applied parallel and perpendicular to the bar surface, are displayed in Fig. 8.2(a) and (b). For the direction of
magnetic field parallel to the sample surface, the external DC field is varied from 0 mT to 270 mT; whereas for fields perpendicular to the sample surface, from 0 mT to 215 mT. They both show that critical current decreases much quicker in the range from 0 to 50 mT.

Fig. 8.1. Bi-2223 bar current lead fabricated by a combination of CIP and sinter forging.

Table 8.1. Transport Properties of a Bi-2223 Current Lead (77 K, Self-field)

<table>
<thead>
<tr>
<th>Dimension (cm³)</th>
<th>Fabrication Method</th>
<th>( I_c ) (A)</th>
<th>( J_c ) (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 × 0.4 × 5.4</td>
<td>Combination of CIP and sinter forging</td>
<td>119</td>
<td>300</td>
</tr>
</tbody>
</table>
Fig. 8.2. I-H curve of the Bi-2223 current lead, measured at 77 K with magnetic field applied (a) parallel and (b) perpendicular to the sample surface.

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A schematic of direction of external field $B$, bar surface, $c$ direction, and effective grain misalignment angle $\varphi_{\text{eff}}$ [4] for the bar current lead is shown in Fig. 8.3. $B \sin(\theta + \varphi_{\text{eff}})$ is the $B$ component along the direction perpendicular to the bar surface. $\theta$ is the angle between field $B$ and bar surface, which is written as

$$B_{//c}(B, \theta) = B \sin(\theta + \varphi_{\text{eff}}) \quad (1)$$

When $\theta = 0^\circ$, i.e., $B$ is parallel to the bar surface, this case corresponds to the $I_c$ ($B // \text{bar surface}$), and Eq. (1) becomes,

$$B_{//c}(B,0^\circ) = B \sin \varphi_{\text{eff}} \quad (2)$$

When $\theta = 90^\circ$, i.e., $B$ perpendicular to the bar surface, this case corresponds to the $I_c$ ($B \perp \text{bar surface}$), and Eq. (1) becomes,

$$B_{//c}(B,90^\circ) = B \sin(90^\circ + \varphi_{\text{eff}}) \quad (3)$$

Because of the 2D behavior of Bi-2223 compound, the dissipation of the samples results only from $B_{//c}$. Thus, the same $I_c$ in the curve $I_c$ ($B // \text{bar surface}$) and $I_c$ ($B \perp \text{bar surface}$) should correspond to the same $B_{//c}$ value. Because $B_{//c}(B, \theta) = B \sin(\theta + \varphi_{\text{eff}})$, and suppose $\varphi_{\text{eff}}$ is a small angle, when $\theta = 90^\circ$, Eq. (3) becomes

$$B_{//c}(B, \theta) = B \sin(90^\circ + \varphi_{\text{eff}}) \equiv B \sin 90^\circ = B \quad (4)$$

This means that the deviation of $I_c$ ($B \perp \text{bar surface}$), caused by grain misalignment, is at a the minimum. So, the curve, $I_c$ ($B \perp \text{bar surface}$) is used as the reference curve. From Fig. 8.4, when $\varphi_{\text{eff}} \leq 15^\circ$, the curve 1, which is converted from $I_c$ ($B // \text{bar surface}$) and now becomes $I_c = I_c$ ($B \sin 15^\circ$), is in good agreement with the reference curve $I_c$ ($B \perp \text{bar surface}$) below 20 mT. When $\varphi_{\text{eff}} = 7.2^\circ$, curve 2, which is converted from $I_c$ ($B // \text{bar surface}$) and now becomes $I_c = I_c$ ($B \sin 7.2^\circ$), is in good agreement with the reference
curve $I_c (B \perp \text{bar surface})$ from 15 to 45 mT. All data for the curves are listed in Table 8.2. Therefore, we believe the effective grain misalignment angle is between $7.2^\circ$ and $15^\circ$.

Fig. 8.3. Schematic illustration of the bulk surface, $B$ direction and effective grain misalignment angle $\phi_{\text{eff}}$ for the bulk Bi-2223 sample.
Fig. 8.4. $I_c (B//\text{bulk surface})$, $I_c (B \perp \text{bulk surface})$, and $I_c$ with $\varphi_{\text{eff}} = 15^\circ$ (curve 1) and $I_c$ with $\varphi_{\text{eff}} = 7.2^\circ$ (curve 2) for the Bi-2223 current lead.
Fig. 8.5. (a) (0010) pole figure for the Bi-2223 current lead fabricated by the CIP and HP method. (b) Average integrated intensity vs $\psi$ calculated from (a), $\psi(50\% \text{ Ave}) = 10^\circ$, $\psi(90\% \text{ Ave}) = 50^\circ$. 

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### Table 8.2. Data lists for Fig. 8.4, where reference curve \((B_{//c}, I_{c/|c|})\), curve 1 \((I_{c//ab}, B_{//ab \ Sin 15^\circ})\), and curve 2 \((I_{c//ab}, B_{//ab \ Sin 7.2^\circ})\)

| \(I_{c//ab}\) (A) | \(B_{//ab}\) (mT) | \(B_{//ab \ Sin 15^\circ}\) (mT), X value for curve 1 | \(B_{//ab \ Sin 7.2^\circ}\) (mT), X value for curve 1 | \(I_{c/|c|}\), Y value for curve 1, curve 2, and reference curve (A) | \(B_{//c}\), X value for reference curve (mT) |
|-------------------|-----------------|---------------------------------|---------------------------------|---------------------------------|-----------------|
| 118               | 0               | 0                               | 0                               | 118                             | 0               |
| 115               | 0.21            | 0.054                           | 0.027                           | 116.5                           | 0.212           |
| 117               | 0.30            | 0.078                           | 0.038                           | 115.5                           | 0.303           |
| 118               | 0.61            | 0.156                           | 0.076                           | 116                             | 0.606           |
| 118               | 1.21            | 0.313                           | 0.152                           | 113.5                           | 1.213           |
| 116.5             | 1.81            | 0.469                           | 0.227                           | 111.5                           | 1.819           |
| 116.5             | 3.03            | 0.782                           | 0.379                           | 105                             | 3.031           |
| 109.5             | 4.85            | 1.251                           | 0.606                           | 83.5                            | 4.850           |
| 90                | 9.70            | 2.500                           | 1.21                            | 53                              | 9.700           |
| 51.5              | 30.92           | 7.980                           | 3.865                           | 39                              | 18.187          |
| 46.7              | 50.32           | 12.98                           | 6.290                           | 30                              | 50.317          |
| 44.5              | 100.03          | 25.81                           | 12.503                          | 25.5                            | 100.028         |
| 43                | 150.35          | 38.79                           | 18.793                          | 21.5                            | 150.345         |
| 36                | 215.21          | 55.53                           | 26.902                          | 15.5                            | 215.212         |
| 35.5              | 272.80          | 70.38                           | 34.100                          |                                 |                 |
8.3.2 Average Grain Misalignment Angle determined by Pole Figure Method and SEM

To investigate the grain misalignment of the HP sample quantitatively, the pole figure of the (0010) peak is measured on the bulk surface after removing the top layer. The result is shown in Fig. 8.5(a). Fig. 8.5(b) shows the curve of intensity vs $\psi$ calculated from Fig. 8.5(a). The average integrated intensity percentage at 50% is around $10^\circ$. It could be understood that this angle corresponds to the average grain misalignment angle $\phi_{av}$, and is consistent with the effective grain misalignment angle $\phi_{eff}$. Although the average grain misalignment angle $\phi_{av}$ is $10^\circ$, the misalignment angle of some grains is much larger, for example, the misalignment angles of 10% of the grains are more than $50^\circ$. These grains with large misalignment angle have very detrimental effect on the transport properties of the current lead. Better textured sample having $J_c$ of 1000 A/cm$^2$ had a small misalignment angle (of $\sim 9^\circ$) [9].

A typical SEM image is shown in Fig. 8.6. From this image, it can be seen that the misalignment angles of some grains are small, less than $10^\circ$. Some grains, however, have large misalignment angles, with the largest around $60^\circ$. This confirms the result of the pole figure, shown in Fig. 8.5. Most of the grains are platelike and the connectivity between grains is good. However, some grains have the cuboid shape, which is detrimental to the transport property of the current leads [5]. In the case of Bi-2223/Ag tape, the effective misalignment angle is of the order of $8^\circ - 9^\circ$ [8] and varies with the tape thickness [5]. Most of the grains are large plates [8]. This one of the main reasons why the critical current density of Bi-2223 bulk is much lower than that of Bi-2223/Ag tape.
8.4. Summary

Bi-2223 bar current leads were fabricated by a combination of cold isostatic pressing (CIP) and sinter forging (HP). The critical currents were measured at 77 K by varying the external DC magnetic field (B), which was applied parallel and perpendicular to the bulk sample surface, i.e., \( I_c (B//\text{bar surface}) \) and \( I_c (B\perp \text{bar surface}) \), respectively. The critical current \( I_c \) and critical current density \( J_c \) were 119 A and 300 A/cm\(^2\), respectively, for the bar current lead (investigated in this chapter) with 0.4 cm thick, 1.0 cm wide, and 5.4 cm long. The effective grain misalignment angle, \( \varphi_{\text{eff}} \), was around 10°, calculated from its \( I_c (B//\text{bar surface}) \) and \( I_c (B\perp \text{bar surface}) \) curves by using a 2D model. For comparison, the average grain misalignment angle, \( \varphi_{\text{av}} \), found in microstructure using SEM, was measured by pole figure. The results obtained were in agreement with the effective grain misalignment angle \( \varphi_{\text{eff}} \). The phases and microstructure were analyzed by XRD and SEM.
References


Chapter 9: Summary and conclusions

This thesis contains the following main points: (1) with improving critical current density in mind, a novel technique, including a combination of cold isostatic pressing and sinter forging, was developed to fabricate Bi-2223 bulks. (2) Prototypes of Bi-2223 current leads with ~ 5 cm in length were prepared using the novel technique, then the properties, critical current density performance and contact resistivity, were characterized. (3) The effect of post annealing in a low oxygen atmosphere on critical current density was also investigated. (4) Electro-magnetic properties and grain alignments for Bi-2223 current lead prototypes were studied separately.

Bi-2223 precursor powders with a small particle size (< 5 μm) and good homogeneity were successfully fabricated using a spray-drying technique. A nominal composition with a cation stoichiometry of Bi:Pb: Sr:Ca:Cu = 1.84:0.34:1.91:2.03:3.06 was used and proved to be a desirable starting composition. The solution of dissolved oxide compounds was spray dried. In order to homogenize the powder, to decrease the particle size and to speed up the reaction rate during powder calcination, the collected blue raw powder was heated slowly to 500 °C at a rate of 3 °C/h, then calcined at 800 °C ~ 820 °C for 5 hours, ground for 1-2 hours and sintered at 800 °C ~ 820 °C for 8 hours. The XRD pattern showed that the original precursor powder was composed of a dominant Bi-2212 phase and other minor phases. DTA measurements indicated that the green precursor powder has an onset melting temperature of about 836 °C. SEM images showed that the green precursor powder has a small particle (below 5 μm) and homogeneous distribution. Particle size
analysis (PSA) showed that ‘spray dry precursor powder” had a mean volume diameter $D_{v, 0.5}$ of 40.5 µm and deceased to 3.9 µm after an additional one hour grinding. This indicated the importance of sufficient grinding in obtaining fine green precursors.

A novel technique involving a combination of CIP and sinter forging was applied to the fabrication of Bi-2223 bulks, and pre-sintering was conducted after (route 1) and before CIP (route 2). The effects of the deformation rate of sinter forging and pre-sintering were investigated. When pre-sintering was conducted after CIP (route 1), the critical current density of bulks at 77 K was much higher than that of bulks made by route 2 (pre-sintering before CIP). Measurements of the field dependence of the critical current density revealed that optimized sinter forging could improve the critical current density $J_c$ behavior in an external field, particularly in the low field region below 50 mT, for the samples where CIP was conducted before pre-sintering. Higher deformation rates of sinter-forging can improve the flux pinning force when the external field is parallel to the sample surface, but degrades the pinning force density when the external filed is perpendicular to the sample surface ($H_{//c}$, 77 K). Samples which were initially pre-sintered and deformed at reduction rate up to 70% have 10 times lower of the pinning force peak than the samples initially subjected to CIP and deformed at a 70% for both directions ($H_{//c}$ and $H_{//c}$, at 77K).

The influence of the sinter-forging rate on critical current density behavior ($J_c$) in an external field and on contact resistance $R_c$ for a prototype Bi-2223 current leads has been investigated. The current leads were fabricated by a combination of Cold Isostatic Pressing (CIP) and sinter-forging methods with the thickness reduction rate ranging from 0% to 90%. The two silver contact ends of each sample were also prepared during the sinter
forging. The results revealed that $J_c$ was strongly affected by the deformation rate of sinter forging and reached a maximum of 725 A/cm² at a deformation rate of 80%, without post annealing. From the measurements of external magnetic field dependence on $J_c$, it was determined that sinter forging could improve $J_c$ behavior in external fields, particularly in the regime below 50 mT. Measurements of contact resistance $R_c$ were conducted for different transport currents at 77 K. Results showed that the contact resistance had a level of $\sim 10^{-6} \Omega$ cm² and for the samples with higher deformation rates showed less dependence on the transport current over a range from 0.5 A to 50 A.

The effects of the deformation rate during sinter-forging and annealing in 7.5 % O₂/ N₂ on critical current density of (Bi, Pb)₂Sr₂Ca₂Cu₃O₇ current leads have been investigated. The samples were prepared by sinter forging 2 or 3 times, cutting each bulk into two longitudinal pieces and then overlaying the two pieces together for next sinter forging. The samples were annealed in 7.5 % O₂/N₂ two times at 825 °C for 24 hours. The maximum critical current density achieved by this technique exceeded 1000 A/cm² at 77 K and self-field. The results revealed that both the sinter-forging deformation rate and annealing in low oxygen atmosphere affected critical current densities significantly.

The electro-magnetic properties of Bi-2223 current leads with critical current density ($J_c$) of 1000 A/cm² at 77K and self-generated magnetic field were investigated. The phases and microstructures were analyzed by XRD and SEM. The texture and weak link behavior were studied by pole figures and AC susceptibility, respectively. The results showed that
the matrix density, grain connectivity and texture were improved significantly by sinter forging.

The grain alignment of Bi-2223 bar current leads with critical current density of 300 A/cm², fabricated using CIP and sinter forging, was studied in a quantitative way. Critical currents were measured at 77 K by varying an external DC magnetic field (B), which was applied parallel and perpendicular to the bulk sample surface, i.e., I_c (B∥bar surface) and I_c (B⊥bar surface), respectively. The critical current I_c and critical current density J_c were 119 A and 300 A/cm², respectively, for a bar current lead with 0.4 cm thick, 1.0 cm wide, and 5.4 cm long. The effective grain misalignment angle, φ_eff, was around 10°, calculated from its I_c (B∥bar surface) and I_c (B⊥bar surface) curves by using a 2D model. For comparison, the average grain misalignment angle, φ_avg, found in microstructure using SEM, was measured by pole figure. The results obtained were in agreement with the effective grain misalignment angle φ_eff.
List of publications during PhD study period (from 1998 to 2001)


