Doctoral Thesis

**Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_8$-$\delta$ high temperature superconductor precursors for power application components**

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**Publication Date:**
2004

**Permanent Link:**
https://doi.org/10.3929/ethz-a-004845434

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$\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{8+\delta}$

High Temperature Superconductor Precursors for Power Application Components

A dissertation submitted to the

SWISS FEDERAL INSTITUTE OF TECHNOLOGY
ZURICH

Switzerland for the degree of
Doctor of Science

presented by

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Zurich, 2004
# Table of Contents

1. Introduction  
   1.1. General overview  
   1.2. The $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8,\delta$ compound  
   1.3. Aim of the work  
   1.4. Layout of the work  

2. Critical Current Densities of Bi-2212 Thick Films Processed from Commercial Precursors  
   2.1. Introduction  
   2.2. Experimental  
   2.2.1. Analysis and critical current densities of commercial precursors  
   2.2.2. Influence of particle aspect ratio and phase composition on the critical current density  
   2.3. Results and discussion  
   2.3.1. Analysis and critical current densities of commercial precursors  
   2.3.2. Influence of particle aspect ratio and phase composition on the critical current density  
   2.4. Conclusions  

3. Influence of Precursor Inhomogeneity on the Critical Current Density of Bi-2212 Superconductors  
   3.1. Introduction  
   3.2. Experimental  
   3.2.1. Analysis of particle size fractions of a precursor  
   3.2.2. Influence of second phases morphology on the critical current density of fully processed Bi-2212.  
   3.2.3. Formation mechanism of large second phase particles
3.3. Results and Discussion 37
   3.3.1. Analysis of particle size fractions of a precursor
   3.3.2. Influence of second phases morphology on the critical current density of fully processed Bi-2212.
   3.3.3. Formation mechanism of large second phase particles

3.4. Conclusions 48

4. Influence of Precursor Calcination Parameters on the Critical Current Density of Bi-2212 Superconductors 51
   4.1. Introduction 52
   4.2. Experimental 55
      4.2.1. Precursor preparation parameters
      4.2.2. Calcination with reduced atmosphere exchange
      4.2.3. Partial melt processing of the calcined precursors
   4.3. Results 58
      4.3.1. Calcination conditions that lead to melt formation
      4.3.2. Calcination with reduced gas exchange
      4.3.3. Influence of heating rate during calcination
      4.3.4. Influence of oxygen partial pressure during calcination on the critical current density of fully processed material
      4.3.5. Influence of calcination temperature on \( j_c \) of partial melt processed Bi-2212
   4.4. Discussion 72
   4.5. Conclusions 74

5. Novel Precursor Reaction Pathways to Bi-2212 Bulk Superconductors 77
   5.1. Introduction 78
   5.2. Experimental 80
   5.3. Results and discussion 84
      5.3.1. Precursor properties
5.3.2. Influence of the precursor phase composition on the critical current density of fully processed Bi-2212

5.3.3. Bi-2212 phase formation during heating to the partial melt state

5.3.4. Peritectic decomposition of the reacted precursors

5.3.5. Influence of precursor phase composition on the microstructures of fully processed Bi-2212

5.4. Summary and Discussion

5.5. Conclusions

6. Enhanced Residual Second Phase Dissolution by Atmosphere Control in Bi-2212 Superconductors

6.1. Introduction

6.2. Thermodynamic considerations

6.3. Experimental

6.4. Results

6.4.1. Influence of annealing temperature and oxygen partial pressure on the critical current density

6.4.2. Influence of temperature and pO₂ on the phase composition

6.4.3. Influence of temperature and pO₂ on microstructure and phase composition

6.4.4. TEM analysis of Bi-2212 quenched from the partial melt state

6.5. Discussion

6.5.1. Crystallization of Bi-2212 from the melt

6.5.2. Microstructure formation during annealing

6.5.3. Critical current densities

6.6. Conclusions

7. Outlook

7.1. Future precursor development

7.2. Future partial melt process optimization
Appendix 1: Starting Powder, Precursor and Processing Specifications 123

Appendix 2: Preparation of Homogeneous Starting Powder Mixtures for Bi-2212 Precursor Production 126

Appendix 3: Influence of Impurity Elements in the Precursor on the Critical Current Density of Partial Melt Processed Bi-2212 130

Acknowledgment 135

Curriculum Vitae 137
Summary

For power applications, such as the fault current limiter, where primarily high current carrying capabilities are required, thick film and bulk material of the high temperature superconductor Bi-2212 have evolved as the most promising for first applications. Such Bi-2212 components are produced by the partial melt process, where the initial precursor component peritectically decomposes to 014x24, 91150 and a melt. From this partial melt state then a percolating network of superconducting Bi-2212 platelets is formed upon cooling.

The aim of this work was to increase the critical current density ($j_c$) of partial melt processed Bi-2212. This was achieved by increasing the effective current carrying cross-section of the components by reducing the amount of residual second phases in the microstructures of processed material. The major second phase is 014x24, which is present as small single particles and as large agglomerates of grains. The latter are a consequence of an inhomogeneous distribution of the peritectic phases in the partial melt state. As only the smaller particles can be proportionally dissolved during the crystallization of Bi-2212, the residual single grains and excessive second phase will remain in the final microstructure. They respectively originate from the large 014x24 particles and agglomerates. Therefore the incomplete dissolution of 014x24 during the crystallization of Bi-2212 upon cooling from the partial melt state is a consequence of an inhomogeneous arrangement and the wide particle size distribution of the peritectic phases in the melt.

In this work the homogeneity of the final product and thus the effective current carrying cross-section was increased by (a) increasing the homogeneity of the partial melt state and (b) by reducing the stability of the 014x24 phase during annealing. The latter was achieved by annealing under reduced oxygen partial pressure at 850°C thereby promoting 014x24 phase dissolution and making way for further Bi-2212 formation. The homogeneity of the partial melt state critically depends on the homogeneity of the precursors and is obtainable when the peritectic decomposition is uniform. A homogeneous partial melt state is typically observed with precursors that have many fine and homogeneously distributed material imperfections and do not have large and perfect Bi-2212 particles with high aspect ratio. This further concluded that certain phase compositions present in the precursors could lead to higher $j_c$ than others. Such precursors were produced by avoiding melt formation during calcination, high calcination temperatures or adjusting unreactive phase compositions.
The result of the study was an increase of the critical current density of bulk and thick film components from around 3000 A/cm² to over 8000 A/cm² at 77 K.

Zusammenfassung

Für Starkstromanwendungen, wie beispielsweise Strombegrenzer, bei denen in erster Linie hohe Stromdichten gefordert sind, haben sich Dickfilm- und Massivbauteile aus Bi-2212 als erfolgsversprechend für erste Anwendungen erwiesen. Solche Bi-2212 Komponenten werden über einen partiellen Schmelzprozess hergestellt. Dabei zerfällt das Pulver des Grünkörpers peritektisch zu $0_{14x24}$, $91_{150}$ und einer Schmelze. Daraus kann sich dann während des Abkühlen ein perkulatorisches Netzwerk aus supraleitenden Bi-2212 bilden.

Das Ziel der Arbeit war die kritische Stromdichte von schmelzprozessiertem Bi-2212 zu steigern. Dies wurde erreicht durch eine effektive Vergrößerung des stromtragenden Querschnitts erreicht, indem der Fremdphasenanteil in der Mikrostruktur des prozessierten Materials verringert wurde. Die Hauptfremdphase ist $0_{14x24}$, die als einzelne kleine Körner oder als grosse Ansammlung von Körnern vorliegen kann. Letztere ist die Folge einer ungleichmässigen Verteilung der peritektischen Phasen im partiell geschmolzenen Zustand. Da sich während der Kristallisation von Bi-2212 nur die kleineren Körner proportional auflösen können, stammen die einzelnen $0_{14x24}$ Körner ursprünglich von grossen Körnern und Agglomeraten im partiell geschmolzenen Zustand. Das unvollständige Auflösen von $0_{14x24}$ während der Bi-2212 Kristallisation kann auf die inhomogene Verteilung der peritektischen Phasen und einer breiten Korngrössenverteilung der Phasen im partiell geschmolzenen Zustand zurückgeführt werden.

In dieser Arbeit wurde die Homogenität des Endprodukts und daher der effektive stromtragende Querschnitt erhöht indem (a) die Homogenität des partiell geschmolzenen Zustands verbessert wurde und (b) die Stabilität der $0_{14x24}$ Phase während des Glühens reduziert wurde. Letzteres wurde durch Glühen in sauerstoffarmer Atmosphäre bei 850°C erreicht, wodurch der Zerfall von $0_{14x24}$ gefördert wurde, was eine weitere Bi-2212 Bildung erleichterte. Die Homogenität des partiell geschmolzenen Zustands hängt direkt mit der Homogenität des Pulvers zusammen, und wird erreicht wenn es einheitlich peritektisch zerfällt. Ein homogener partiell geschmolzener Zustand wird typischerweise beobachtet mit Pulvern die viele feine und homogen verteilte Fehlstellen haben und keine grossen und perfekten Bi-2212 Plättchen mit hohen...
Formfaktoren. Das heisst, dass gewisse Pulver-Phasenzusammensetzungen Bi-2212 Bauteile mit höheren \( j_c \) ergeben werden als andere. Solche Pulver wurden hergestellt indem die Bildung von Schmelze während des Kalzinierens und hohe Kalziniertemperaturen vermieden wurden, oder durch die Kombination von unreaktiven Phasenpaaren.

Als Folge dieser Schritte wurde die kritische Stromdichte von Massiv- und Dickfilmkomponenten von rund 3000 A/cm\(^2\) auf über 8000 A/cm\(^2\) bei 77 K gesteigert.
Table of Nomenclature

1. Common Terms

<table>
<thead>
<tr>
<th>Term</th>
<th>Abbreviation</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td></td>
<td>Powder product from which a Bi-2212 ceramic is processed</td>
</tr>
<tr>
<td>Critical current density</td>
<td>$J_c$</td>
<td>Defined at given voltage drop per length of conductor, based on its I-V characteristic</td>
</tr>
<tr>
<td>1 or 10 $\mu$V/cm criteria</td>
<td></td>
<td>Voltage drop per length commonly used to define $J_c$</td>
</tr>
<tr>
<td>Current carrying cross-section</td>
<td></td>
<td>Effective area of the superconductor that can carry super currents, which is typically &lt; real conductor cross-section</td>
</tr>
<tr>
<td>Critical temperature</td>
<td>$T_c$</td>
<td>Temperature below which a superconductor becomes superconductive</td>
</tr>
<tr>
<td>Oxygen partial pressure</td>
<td>$P_{O_2}$</td>
<td>Oxygen content in the gas atmosphere concerned, expressed as fraction with a total pressure of 1 bar</td>
</tr>
<tr>
<td>Second phases</td>
<td></td>
<td>Phases other than Bi-2212 present in a Bi-2212 HTS</td>
</tr>
<tr>
<td>Particle</td>
<td></td>
<td>Single or poly crystal in a precursor</td>
</tr>
<tr>
<td>Grain</td>
<td></td>
<td>Primary particle in a precursor or individual crystals in a microstructure</td>
</tr>
<tr>
<td>Partial melt process</td>
<td>PMP</td>
<td>A heat treatment typically used for processing HTS, through which a precursor is sintered and crystallized to a dense and superconducting component</td>
</tr>
</tbody>
</table>

2. Common Phases

<table>
<thead>
<tr>
<th>Phase</th>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$Sr$_2$Ca$_4$Cu$_2$O$_8$</td>
<td>Bi:2212</td>
<td>High $T_c$ compound, 2 CuO layers</td>
</tr>
<tr>
<td>Bi$_2$Sr$_2$Cu$_1$O$_6$</td>
<td>2201</td>
<td>Low $T_c$ compound, 1 CuO layers</td>
</tr>
<tr>
<td>Bi$_4$Sr$_4$Ca$_1$Cu$_3$O$_4$</td>
<td>&quot;4413&quot;</td>
<td>Random mix of the 1 and 2 layered compound</td>
</tr>
<tr>
<td>Bi$_2$Sr$_1$O$<em>6$Cu$</em>{0.4}$Cu$_1$O$_6$</td>
<td>22x1</td>
<td>Composition of the peritectic liquid (melt) and a 2201 modification</td>
</tr>
<tr>
<td>Sr$_{14-x}$Ca$_x$Cu$<em>2$O$</em>{38}$</td>
<td>014x24</td>
<td>Bi-free peritectic second phase</td>
</tr>
<tr>
<td>Bi$<em>4$Sr$</em>{11}$Ca$<em>5$O$</em>{30}$</td>
<td>91150</td>
<td>Cu-free peritectic second phase</td>
</tr>
</tbody>
</table>
Nomenclature: Bi-2212 High Temperature Superconductor Precursors for Power Application Components
Introduction

1. General overview

High temperature superconductors are ceramic materials. Their no-ductivity makes it difficult to process them to long length and flexible conductors with a narrow distribution of the properties as required for most applications. It becomes obvious that it is to incorporate such HTS into superconducting devices and even worse, the materials have intrinsic limitations like bad pinning properties against magnetic fields and weak links between the grains at liquid N₂ temperature.

Despite these drawbacks, many technical and fundamental achievements were made in the last 5 years in the area of high temperature superconductors. In the following the most prominent shall be named: (a) Research on the grain boundaries of the compound YBCO has led to the understanding of the origin of the weak link behaviour and presented possible solutions [1]. The YBCO crystal reduces grain boundary stress by oxygen depletion towards the grain boundary. As the superconducting properties are very sensitive towards the oxygen content and due to the low coherence length of only a few Å, this depletion leads to strongly reduced superconducting properties in the grain boundary. Improvements were achieved by doping the grain boundaries with Ca, which however, on the other hand leads to a local reduction of the critical temperature. Therefore, all research is focusing on reducing the number of grains, increasing grain overlapping and relying on thin films approaching single crystal material. (b) A remarkably high critical temperature of 39K was found in the very simple, well known, easy and low cost compound MgB₂ [2]. (c) Large progress was made in the production of first (Bi,Pb-2223) and second generation (YBCO) high temperature superconductor wires/tapes with respect to long length, current carrying
capability and homogeneity of the properties. Wires of Ag sheathed Bi,Pb-2223 can be produced to lengths of several km that can carry currents of 185 A at 77K in self-field (250 μm thick and 4 mm wide) by the powder in tube technique and over pressure annealing [3]. Second generation wires of 10 m have been made of YBCO that achieve currents of 125 A in films (100 μm thick, 4 mm). Because the thickness of the superconducting material in these films is only 3 to 5 μm, YBCO conductors still have large development potential [4]. It can be speculated that second generation wires could lead to the breakthrough for high temperature superconductors due to the high current carrying properties and possibly lower production costs, if the production rate can be increased. First generation conductors will always stay costly due to high cost Ag sheathing.

Wires are needed in many applications, and since Bi-2223 and Bi-2212 wires are available with reasonable properties and in long lengths, several prototypes have recently been built and successfully tested [5]. Besides several cables for power transmission [6], current stabilizing devices [7] and fault current limiting devices [8] were built that can stabilize a power grid. Motors of up to 5000 HP [9] were produced mainly for naval applications and magnets [10] with fields of up to 30 T [11] for analytical applications were set in place.

The present work contributes to the material processing and properties of Bi-2212 for the resistive current limiter of ABB Switzerland. During this work a 6.4 MW prototype was successfully tested and a 10 MW demonstrator that will run in the grid is currently being built [12],[13].

Of the many high temperature compounds discovered in the last 15 years only 3 have found their way to practical power application: YBCO, Bi-2223 and Bi-2212. The three main requirements the compounds have to fulfil for industrial application are: A critical temperature above 77K, the boiling point of liquid nitrogen, high current carrying capabilities and up scalable process with no poisonous elements involved. Each of the compounds listed has a critical temperature over 77 K. However their current carrying properties and production methods differ. YBCO, as noted above, forms weak links between the grains but has good pinning properties and a critical current density of over $2 \times 10^6$ A/cm$^2$ at 77 K [14]. Therefore this material has to be processed in form of thin films with very little grain misalignment or in form of single crystals. On the other hand, Bi-2212 does not form weak links but has very poor pinning properties at 77 K and relatively low critical current densities compared to YBCO. Therefore this material has to be processed to thick films and bulk material which then can carry high currents as required for power...
applications. Finally Bi-2223 has a higher critical temperature of 110 K but is affected by weak links as YBCO is. As this material cannot be melt processed, a high degree of texture is achieved by rolling deformation as done in the powder in tube process [15].

2. The Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_{8+\delta}$ compound

In the system Bi-Sr-Ca-Cu-O at least three superconducting compounds are known. The one layer compound Bi-2201 with a critical temperature of 30K, the two layer compound Bi-2212 with a critical temperature of 95K and the three layers Bi-2223 with a critical temperature of 110K.

The crystal structure of these superconducting compounds are all built up in the same manner. Between the two insulating blocks of Bi, Sr and O in a NaCl structure are 1-3 superconducting CuO layers which are separated by Ca ions. The consequences of this layered structure is reflected in the very anisotropic properties of the compounds. Bi-2212 for instance can conduct about 1000 times more super-current in-plane (a,b) than perpendicular to the CuO planes (c directions). Also the coherence length (distance between the cooper pairs) is 4 nm in plane and just 0.07 nm through the insulating blocks in c direction [16]. The consequence of these anisotropic superconducting properties is that super-currents only flow in-plane. Also the Bi-2212 crystal growth is anisotropic. The crystals grow much faster in-plane than in the c direction, resulting in the formation of grains with platelet morphology.

Bi-2212 can be processed to thick film and bulk material with high critical current densities because percolating networks of strongly coupled grains are formed during the partial melt process. In the superconducting state the currents then will meander along these grains through the material [17], [18]. This behaviour can be described by the parallel-path model found for Bi,Pb-2223 conductors [19], [20]. According to this model the material consists of a strongly-linked backbone which is embedded in a weak-linked matrix. However in contrast to Bi,Pb-2223 this strongly-linked backbone can form during the crystallization of Bi-2212 upon cooling from the partial melt state. Bi-2201 can be partial melt processed as Bi-2212. But as this phase has a critical temperature below 77K it is not of interest for industrial applications.

The production of Bi-2212 thick film or bulk components always starts with a powder of which a green body is formed. The microstructure is densified by the partial melt process. Although each of the Bi-2212 powder particles is superconducting, a super-current cannot pass through the
green body as the grains are not connected with each other in-plane by small angle grain boundaries. Percolating networks that can carry the super-current though the macroscopic component are formed only by partial melt processing, where Bi-2212 grains crystallize from the melt. During the partial melt process [21]-[24], shown in FIGURE 1, the powders peritectically decompose to the solid phases 014x24 and 91150 and a melt [25] as illustrated in FIGURE 2. This partial melt state is not homogeneous as shown in the microstructure quenched from it. The solid phases are unevenly spread and their size distribution ranges from 5 μm to more than 40 μm. From this state, the new Bi-2212 platelets have to precipitate upon cooling from the melt, and have to form a percolating network. The difficulties forming such a percolating network are obvious when inspecting the microstructure of quenched samples during the crystallization of Bi-2212 (see FIGURE 2). The larger peritectic second phases, especially 014x24, cannot react fast enough with the melt to dissolve and enable Bi-2212 crystallization. They are consequently present as residual second phases in the microstructures of the fully processed material, where they reduce the current carrying cross-section, interrupt percolating networks and retain the elements needed for the complete crystallization of Bi-2212. The incomplete inverse peritectic reaction of the solid phases with the melt to Bi-2212 is the reason for the long annealing times applied during the partial melt process after the crystallization of Bi-2212 [24].

Figure 1: Temperature-time sequence of the partial melt process as applied in this work.
Due to this reverse peritectic reaction, the prerequisite for Bi-2212 components with high
current carrying cross-sections and thus high critical current densities $j_c$ is a homogeneous high
temperature state. This homogeneity is required on a microscopic length scale of several micro¬
meters up to the macroscopic scale of the component size, as for instance plates of $40 \times 25$ cm are
processed for fault current limiter application [13]. In order to form a macroscopic percolating
network of Bi-2212 platelets through the component, the nucleation and growth of Bi-2212 must
be able to occur at the same time and find same conditions in the whole material.

![Phase Diagram and Microstructures](image)

**Figure 2:** Simplified phase diagram of a peritectic decomposition of Bi-2212 and the
 corresponding microstructures quenched during the partial melt process.
(L...liquid, S... 014x24 + 91150 solid phases)

In previous work it was shown that the reduction of homogeneity in the partial melt state
leads to fully processed Bi-2212 components with reduced $j_c$. The homogeneity of the partial melt
state depends on one hand strongly on the maximum temperature [23], [25] and on the other on
the annealing time [24], [26]. The influence of the maximum processing temperature on $j_c$ of fully
processed material is shown in FIGURE 3a. At low processing temperatures only small amounts of
melt form with the consequence that the material cannot become dense, percolating networks of novel Bi-2212 that crystallize from the melt are only partially established and thus \( J_c \) is low. At high processing temperatures Ostwald ripening of second phases occurs with the consequence that these large grains can only be partially dissolved during crystallization and thus reduce the current carrying cross-section and \( J_c \). Optimum \( J_c \) are found between these two conditions.

That the sensitivity to the maximum processing temperature can be correlated to the current carrying cross-section is indicated by FIGURE 3b. The \( J_c \) of the samples that were processed at different maximum temperatures were measured at temperatures below 77 K. The results show that \( J_c \) increases for all the samples and that the \( J_c \) values do not merge towards lower temperatures. The \( J_c \) in Bi-2212 is determined by several factors: Grain boundaries (weak links), magnetic effects (flux pinning), the current carrying cross-section of the material and the purity of the phase. The charge carrier density can be neglected as only the maximum temperature was varied and all the other processing steps are the same. The effect of grain boundaries (weak links) and magnetic resistance (flux pinning) both decline with decreasing temperature and would result in a merging of \( J_c \) data of the samples. Therefore these effects can be ruled out and the sensitivity of \( J_c \) towards the maximum temperature can only be attributed to the microstructure, like the current carrying cross-section and the phase purity.
Figure 3: The critical current density $J_c$ of fully processed Bi-2212 in dependence of the maximum processing temperature (upper diagram). $J_c$ of these samples was then measured over a wide temperature range (lower diagram) [23]. To the Bi-2212 precursor used in this work 4wt\% Ag$_2$O was added. Ag reduces the melting temperature of Bi-2212 by 13°C [27],[28].

A similar sensitivity of $J_c$ is found regarding the annealing times in the partial melt state. Too short or too long annealing times result in low $J_c$. The microstructures of samples quenched from the partial melt state that were annealed for short times (20 min at 895°C) have unevenly densified
and are still in the green body state. This indicates that the peritectic decomposition did not occur uniformly throughout the sample. The microstructures of material quenched after long annealing times are dense and the second phase particles are larger, due to Ostwald ripening. Long annealing times should be avoided due to Bi evaporation [29]. Annealing times of 2 hrs showed best results.

Both, the sensitivity of \( J \) towards the maximum temperature and the annealing time, can be explained by referring to the homogeneity of the partial melt state. The latter is only at its maximum when the Bi-2212 component is processed in a narrow temperature range of maximum temperature and for the right annealing time. Processing parameters deviating from this optimum maximum will lead to reduced current carrying cross-section and low \( J \). All annealing steps after the Bi-2212 crystallization [FIGURE 1] are performed to restore homogeneity in the material and increase the current carrying cross-section.

Latter two examples show how important it is to achieve and maintain homogeneity in the partial melt state and by which means it can be decreased. However, it is still unclear how the homogeneity of the partial melt state can be increased.

The hypothesis prior to this work was that the precursor determines the initial homogeneity of the partial melt state. Only from a uniformly decomposing precursor a spatial homogeneous distribution of second phases particles can be expected. This hypothesis, the influence of the precursor on the partial melt state, is not so obvious as all precursors of a nominal Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry (a) react to the Bi-2212 phase during heating to the maximum temperature independent of the initial phase composition and (b) then peritectically decompose to around 40 vol\% oxide melt and 40 vol\% 91150 and 20 vol\% 014x24. Due to the high volume content of melt, one could expect rapid homogenization of any inhomogeneities in the material in the high temperature state. This is however not the fact. Several reports [30], [31] show that the microstructure of the high temperature state, as well as that of fully processed Bi-2212 and its properties are strongly influenced by the precursor properties.
3. Aim of the work

The aim of this work was to increase the critical current density $j_c$ of partial melt processed Bi-2212 components by increasing the current carrying cross-section and to understand the role of precursor properties on the final $j_c$. This was accomplished by two approaches: (a) Increasing the homogeneity of the partial melt state by the development of novel precursors (b) Enhancing the dissolution of residual second phases by reducing the phase stability of the residual $\text{Bi}_4\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_{8+\delta}$.

4. Layout of the work

4.1. Development of novel precursors

To elucidate the influence of the precursor properties on the microstructure and $j_c$ of partial melt processed material, several commercial Bi-2212 precursors were analysed. The results of this work are presented in Chapter 1. It was found that large peritectic second phase particles in the precursor have a deteriorating effect on $j_c$ of fully processed material. Chapter 2 describes the manner how these particles reduce $j_c$ and how they were formed. The results show that any premature melt formation prior to the peritectic decomposition can lead to the formation of these large particles. Therefore the conditions under which melt is formed during calcination was investigated. Its consequences on precursor homogeneity and $j_c$ of partial melt processed samples are presented in Chapter 3. In this study it was found that samples processed from partially reacted precursors yield higher $j_c$ than fully reacted Bi-2212 phase precursors. Therefore precursors of nominal Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry with different phase compositions were prepared and their reactivities were studied during heating to the partial melt state. In Chapter 4 the reactivity of the precursors is correlated with the $j_c$ achieved from the as processed partial melt processed samples.

4.2. Dissolution of residual second phases

After crystallization of Bi-2212 upon cooling from the partial melt state there are always residual peritectic $\text{Bi}_4\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_{8+\delta}$ grains present in the microstructure. During the phase annealing at 850°C in oxygen atmosphere this phase only dissolves very sluggishly. From thermodynamic calculations [32], [33] it could be shown that the stability of this phase decreases at lower oxygen partial pressures $p_{O_2}$. In Chapter 5 the influence of phase annealing in an atmosphere with reduced $p_{O_2}$ on the dissolution of residual $\text{Bi}_4\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_{8+\delta}$ and $j_c$ is demonstrated. This resulted in increased $j_c$ suggesting a higher current carrying cross-section.
References


[3] Larbalestier et al., Wisconsin Superconductor Centre and American Superconductor


Chapter 1

Critical Current Densities of Bi-2212 Thick Films Processed from Commercial Precursors

Abstract

High quality stoichiometric Bi-2212 precursors purchased from commercial producers were analysed and samples thereof partial melt processed. The critical current densities \( j_c \) achieved were between 3000 and 5000 A/cm\(^2\), despite identical processing sequence including the peritectic decomposition to the high temperature phases and consequent crystallization to Bi\(_2\)Sr\(_2\)Ca\(_1\)Cu\(_2\)O\(_{8+d}\) (Bi-2212). A series of powder properties that influence \( j_c \) in the final product were found. The heating rate in the temperature range 550 - 850°C, when heating to the partial melt state, has a strong influence on the \( j_c \) of the fully processed material. This behaviour could be correlated to particle growth and the reduction of precursor imperfections that acting as nuclei for the peritectic decomposition.
1.1. Introduction

The production of high temperature superconducting thick film and bulk components of Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_{8+y}$ (Bi-2212) is based on processing of precursor materials. In the partial melt process the green bodies of Bi-2212 precursor are heated above the peritectic decomposition temperature (892°C) to the partial melt state from which Bi-2212 crystallizes upon cooling down. The phase composition in the partial melt state is Bi$_9$Sr$_{11}$Ca$_5$O$_{30}$ (91150), Sr$_9$Ca$_5$Cu$_{24}$O$_{38}$ (014x24) and a melt. This phase composition in amount of phases and their chemical compositions is close to equilibrium [1]. As the melt has a volume content of around 40%, enabling rapid diffusion, a homogenisation and a state close to the thermodynamic equilibrium can be expected. Therefore the properties of fully processed material should no longer be dependent on precursor properties like grain size and second phase content but mainly on the precursor purity and stoichiometry. However several results point out that the final critical current density $j_c$ of Bi-2212 components is highly depending on precursor properties and that the partial melt state does not “reset the history” of a precursor [2], [3], [4]. A lot of work has been done in correlating precursor properties of powder in tube processed Bi(Pb)-2223 with the critical current density [5], [6], [7]. The influence of the precursor on the final device properties is reasonable as this material is processed with much less melt than the Bi-2212 and therefore is far from thermodynamic equilibrium.

Only very little is known about the influence of precursor properties of stoichiometric Bi-2212 precursors on the $j_c$ of fully processed material. Recent work has shown that second phase particles survive the partial process [4] and that phase composition and particle morphology [8] have an influence on the transition to the partial melt state. In this work we show the strong influence of precursor properties on the $j_c$ of fully processed Bi-2212 using commercial precursors. Identically partial melt processed samples show wide scattering of $j_c$. The aim of this work is to describe different reasons from which this could originate. The precursors were characterized by various techniques. The influence of particle size and phase composition on the final $j_c$ were studied on precursors produced by the same producers by applying different heating rates during heating up to the peritectic decomposition temperature.
1.2. Experimental

1.2.1. Analysis and critical current densities of commercial precursors

There are several commercial stoichiometric Bi-2212 high quality powder products on the market. The precursors are produced by solid state reaction (Solvay SBS), co-precipitation (Target Materials SCC), melting of the starting substances (Nexans Nex3 and Nex1) and processed by spray pyrolysis (Merck Merck, Merck sub and Praxair PA). All precursors were purchased in the year 2000. Their particle size, surface area and specifications are listed in Table 1. In the first part of this work only the fully reacted conventional precursors (SBS, Merck; PA, SCC and Nex3) will be compared.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>d50 [μm] *</th>
<th>BET [m²/g] †</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBS</td>
<td>6.73</td>
<td>1.161</td>
<td>SLB 20, 320-1</td>
</tr>
<tr>
<td>Merck</td>
<td>2.35</td>
<td>3.785</td>
<td>TP435522</td>
</tr>
<tr>
<td>Merck sub</td>
<td>1.07</td>
<td></td>
<td>TP447206</td>
</tr>
<tr>
<td>PA</td>
<td>3.65</td>
<td>2.44</td>
<td>03-IPB2158BM.B.02</td>
</tr>
<tr>
<td>SCC</td>
<td>2.74</td>
<td>1.531</td>
<td>5248scp3</td>
</tr>
<tr>
<td>Nex1</td>
<td>2.68</td>
<td></td>
<td>SLP42 1</td>
</tr>
<tr>
<td>Nex3</td>
<td>2.26</td>
<td>6.662</td>
<td>SLP42 3</td>
</tr>
</tbody>
</table>

Table 1: Grain size, surface area of the precursors and the critical current density of fully processed material. * X-ray disc centrifuge (XDC) with a Brookhaven Instrument Cooperation, † Measured by N₂ adsorption method (BET) with a QuantaChrome Nova1000.

All the precursors, except Nex1, are of Bi-2212 phase composition and therefore must have been calcined at temperatures above 800°C. This temperature is needed in order that phase pure Bi-2212 can form, independently of which starting material and mixing technique had been used.

Samples were partial melt processed from the precursors. The sample processing and partial melt process (Figure 1) is the same for all precursors. For each experiment five samples of each precursor were processed by uniaxially pressing (250 MPa) the precursor in an Ag crucible. The sample dimensions were 13 mm in diameter with an initial thickness of 700 μm and a final thickness of around 400 - 500 μm after partial melt processing.
Chapter 1: Critical Current Density of Bi-2212 Thick Films Processed from Commercial Precursors

Figure 1: Temperature, time and atmosphere program of the partial melt process used in this study. The normal maximum temperature used is 895°C and heating rate between 550 and 850°C is 180°C/hr. For the specific experiments the maximum temperature and the heating rates were varied.

The critical current density $J_c$ of the processed samples is measured with an AC-magnetometer, using the 10 μV/cm criteria ($J_c$ is about 30% higher than measured with the 1 μV/cm criteria).

1.2.2. Influence of particle aspect ratio and phase composition on the critical current density

The effect of particle size was studied on single phase Bi-2212 precursors with a $d_{50}$ of 2.35 μm (Merck) and a $d_{50}$ of 1.07 μm (Merck sub) both produced by Merck.

The effect of phase composition was studied on a fully reacted precursor (Nex3, $d_{50}$=2.26 μm) and its unreacted melt quenched source (Nex1, $d_{50}$=2.68 μm) both produced by Nexans. Samples were processed at different heating rates between 550 and 850°C in flowing oxygen during heating up to the partial melt state during processing. The heating rates are: 20, 60, 120, 180 and 240°C/hr as shown in Figure 1. The SBS precursor was used as a reference. Additionally samples were heated with 180°C/hr and annealed for 3 hrs at 850°C before following the normal partial melt process. The latter experimental conditions were chosen in order to check whether slow heating ramps are equivalent to longer annealing times.
1.3. Results and discussion

1.3.1. Analysis and critical current densities of commercial precursors

In Table 1 the grain size and surface area of the conventional precursors are listed. The $d_{50}$ of the precursors range from 2 to 9 $\mu$m corresponding to surface areas of 6.7 and 1.2 m$^2$/g respectively. The critical current densities $j_c$ of the partial melt processed samples are listed in Table 2. The $j_c$ differed between the precursors more than 2400 A/cm$^2$ for the samples processed at a maximum temperature of 895°C. The highest values were achieved from the solid state reacted powder. XRD analysis of the precursors showed that the main phase in all specimens is Bi-2212. The second phases are also the same: 2201 and peritectic second phases $\text{014x24}$, $\text{91150}$. Their amounts however, varied substantially as shown in Figure 2. The XRD data were quantified by the Rietveld approach using the TOPAS software. The 2201 second phase contents ranged from 1.67 to 4.82 wt% for the spray pyrolysis precursor Merck, and the melt quenched precursor Nex3 respectively. The $\text{014x24}$ second phase contents ranged from 3.67 to 10.4 wt% for the co-precipitated precursor SCC and the melt quenched precursor Nex3 respectively. The $\text{91150}$ contents ranged from 0.62 to 1.88 wt% for the melt quenched precursor Nex3 and the spray pyrolysis precursor PA respectively.

![Figure 2: Quantitative analysis of second phase content in the precursors by the Rietveld method using TOPAS. (XRD, 2 theta measurements, Cu-κα, Bruker D-5000)](image)
SEM micrographs of mounted and polished green bodies are shown in FIGURE 3. Besides the fine Bi-2212 grains there are large particles consisting of Cu and Sr-rich second phases (dark particles). In the PA precursor, many large second phase particles of around 50 μm in diameter were present. In the SCC precursor there were very large (100 μm) particles consisting of 014x24 and some Bi-2212-2201 platelets originating from melt that must have formed during calcination, besides the very fine (1 μm) Bi-2212 particles. Although Nex3 has high contents of second phases, their particles were smaller and more homogeneously distributed. In the Merck precursor the least second phase particles with large diameters were found. Core-shell particles were only found in the SBS precursor[4].

![SEM micrographs](image)

Figure 3: SEM micrographs (backscatter mode) of mounted and polished green bodies. The black matrix is the mounting resin, the fine particles Bi-2212, the dark big blocks are Sr- and Cu-rich phases and the bright Bi-rich phases.

The large amounts of 014x24 and 2201 found in the melt quenched precursor Nex3 can be related to the production method of this precursor. In quenched amorphous material of nominal Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry, 2201 is the first phase to crystallize upon calcination [11], [12] and 014x24 or 01x1 are already present in the quenched material as they are high temperature phases. No direct correlation between the production method and the amount of second phases was found for the other precursors. However the micrographs of the precursors show that the Bi-free
second phase $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{x+4}$ detected by XRD is generally not homogeneously distributed in the precursor, but distributed as big particles in the material. It has been shown [4] that these large $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{x+4}$ particles persist in melt processed material and are especially detrimental to $J_c$.

The DSC measurements (Netzsch STA449C Jupiter, 10°F/min, 40 mg precursor, referenced) of the precursors are presented in FIGURE 4. Two main peaks can be distinguished and correspond to the peritectic decomposition of Bi-2212 around 890°C to $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{x+4}$, 911°C and a melt and the decomposition of $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{x+4}$ around 920°C to $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{x+1}$. Despite all samples consisting of Bi-2212 phase composition, all precursors showed differences in the heating up and the peritectic decomposition behaviour.

During heating up to 890°C all precursors, except the solid state reaction produced precursor SBS, show exothermic behaviour. Merck and PA show just a slight exothermic drift, whereas latter precursor has additionally two endothermic peaks at 300 and 750°C. Both peaks cooccur with a weight loss registered by the TG measurement (not shown here), and therefore originate from a decomposition reaction such as hydroxide or oxalate decomposition at 300°C and carbonate decomposition and/or melt formation at 750°C. Nex3 and especially SCC show a broad and exothermic shallow signal between 600 and 850°C. As no weight loss is registered, this blurred exothermic signal cannot be attributed to carbon burn out.

The precursors can be classified into two groups concerning their peritectic decomposition behaviour and temperatures. A sharp transition is found for SBS, Merck and SCC with onset decomposition temperatures of 889.5°C for SBS, 894°C for Merck and 897°C for SCC. The other two precursors Nex3 and PA decomposed at lower temperatures 886°C and 887°C and the transitions are broad and flat. Reasons for this low energy transition can be found in the relatively high amounts of $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{x+4}$ (Nex3 and PA) in the precursors (FIGURE 2) and in the early melt formation in the PA precursor. The differences in peritectic decomposition are very distinct and can be correlated with the different $J_c$ achieved with the processed samples.

Work by Lang et al. [9], [10] had shown that $J_c$ is very sensitive to the maximum processing temperature ($T_{\text{max}}$). Therefore the precursors were partial melt processed at maximum temperatures of 891, 895 and 899°C. The resulting $J_c$ are presented in TABLE 2 showing that independent of the onset decomposition temperature highest $J_c$ were achieved with a maximum processing temperature of 895°C.
The transformation of $\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_8$ to $\text{Bi}_2\text{Sr}_2\text{Cu}_3\text{O}_{7-\delta}$ characterized by the pronounced peak at 920°C in the DSC signal is very uniform for all precursors except for PA. A possible explanation for its broad peak is that some of its $\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_8$ grains are very large and compact and therefore transform more slowly.

Figure 4: High resolution DSC analysis of the commercial precursors in oxygen with a heating rate of 10°C/hr. The insert is an enlargement of the peritectic decomposition around 890°C and the transformation of $\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_8$ to $\text{Bi}_2\text{Sr}_2\text{Cu}_3\text{O}_{7-\delta}$ at 930°C.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SBS</td>
<td>890</td>
<td>3720</td>
<td>5384</td>
<td>5020</td>
</tr>
<tr>
<td>Merck</td>
<td>894</td>
<td>3910</td>
<td>5310</td>
<td>4380</td>
</tr>
<tr>
<td>PA</td>
<td>887</td>
<td>1640</td>
<td>2950</td>
<td>1630</td>
</tr>
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<td>SCC</td>
<td>897</td>
<td>2780</td>
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<td>2970</td>
</tr>
<tr>
<td>Nex3</td>
<td>886</td>
<td>1690</td>
<td>4569</td>
<td>2800</td>
</tr>
</tbody>
</table>

Table 2: Onset temperature of the peritectic decomposition measured by DSC/TG and the critical current density $j_c$ of the precursors partial melt processed at different maximum temperatures.
Despite the fact that all precursors were stoichiometric Bi-2212, consisted of Bi-2212 phase and had second phases contents between 10 and 20 vol%, the $J_c$ of the corresponding fully processed samples varied over more than 2400 A/cm$^2$. A correlation could not be found between $J_c$ and the average grain size ($d_{50}$), the surface area and the amount or nature of the second phases present in the precursors. However the different melting behaviour of the precursors and the large size of second phase particles are known reasons for the different $J_c$. A precursor for which both criteria apply is PA, with its broad peritectic decomposition at lower temperatures compared to the other precursors and its large second phase particles. Consequently the resulting $J_c$ of the processed material is rather low. In contrast, the Merck precursor shows a narrow peritectic decomposition temperature range and has no large second phase particles. Therefore its fully processed material yields high $J_c$.

During heating up to 850°C the DSC measurements already showed differences in the precursors. The heating up to the high temperature state during partial melt processing is equivalent to a second calcination treatment. Previous work [8] has shown that calcination parameters of a precursor have a strong influence on $J_c$, especially the heating rate between 550 and 850°C. Precursors with different phase compositions (Nexland Nex3) and particle sizes (Merck and Merck sub) are available from Nexans and Merck precursors of different phase composition and grain size. By varying the heating rate the subtle effects of phase composition or grain size can be shown.

1.3.2. Influence of particle aspect ratio and phase composition on the critical current density

The influence of grain size and phase composition of the precursor on the critical current density $J_c$ of partial melt processed samples can be studied with the precursors of Merck and Nexans. Merck and Merck sub are both single phase Bi-2212 precursors with the only specified difference being the particle size. Nex3 and Nex1 both have particle sizes around 2.5 μm but differ strongly in phase composition.

The different $J_c$ of samples processed from these precursors is listed in TABLE 3 and shows the effect of precursor phase composition and grain size. To elucidate the origin of this strong effect the samples were heated with different rates in the temperature range 550-850°C and annealed at 850°C during the partial melt process. The intention of this heat treatment was to find the conditions under which the precursor Merck sub and Nex1 respectively behave in the same manner as Merck and Nex3 respectively. The heat treatment will cause the particles to grow and the phase composition transform to Bi-2212.
Table 3: Critical current density of samples processed from different particle sizes (Merck, Merck sub) and phase composition (Nex3, Nex1). The samples were heated with 180°C/hr to 850°C and annealed for 0.1 or 3 hrs.

<table>
<thead>
<tr>
<th>Annealing time [hr]</th>
<th>Merck  [A/cm²]</th>
<th>Merck sub [A/cm²]</th>
<th>Nex3  [A/cm²]</th>
<th>Nex1  [A/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>5310</td>
<td>5635</td>
<td>4569</td>
<td>6074</td>
</tr>
<tr>
<td>3</td>
<td>4852</td>
<td>5391</td>
<td>3030</td>
<td>4205</td>
</tr>
</tbody>
</table>

In FIGURE 5 the \( j_c \) of partial melt processed samples of the different precursors is shown in dependence of the heating rate between 550 and 850°C during heating to the high temperature state (895°C). The highest \( j_c \) were achieved with heating rates of 180°C/hr for all precursors. The results indicate that the heating during the partial melt process is equivalent to an additional calcination heat treatment. This is supported by the results presented in TABLE 3, where the samples were heated with 180°C/hr and then annealed at 850°C for 3 hrs. The resulting \( j_c \) are between 2 and 60% lower indicating that the additional annealing time at high temperatures are responsible for the decay of \( j_c \).

Although the fully reacted precursors SBS, Merck and Nex3 are believed to be unreactive in the temperature range 550°C to 850°C, heating with 20°C/hr leads to 40% lower \( j_c \) than heating with 180°C/hr. The decrease of \( j_c \) for heating rates higher than 180°C/hr can be attributed to the formation of a transient melt and the consequent loss of homogeneity. The decrease of \( j_c \) for lower heating rates will be discussed separately regarding particle growth for the Merck precursors and phase composition for the Nexans precursors.
Figure 5: Critical current density $j_c$ in dependence of the heating rate between 550 and 850°C during partial melt processing. The process before and after this temperature range is identical for all samples.

Influence of particle aspect ratio: Although the particle sizes ($d_{50}$) of the precursors Merck and SBS differ by a factor of nearly 3, the $j_c$ of samples processed from them are about the same. This fact points out that it is not the particle size that has to be regarded as important factor but the aspect ratio of the particles. The decay of $j_c$ with decreasing heating rates and annealing times can therefore be attributed to the change in particle aspect ratio and not to an uniform particle growth. This is also supported by the anisotropic growth of the Bi-2212 platelets. If the samples of Merck sub are heated with a heating rate of 60°/hr they have the same $j_c$ as samples of Merck heated with 180°/hr. A heating rate of 60°/hr corresponds to a prolonged heat treatment of 33 min in the temperature range 800-850°C, in which a strong anisotropic particle growth can be expected, compared to a heating rate of 180°/hr. During this period the aspect ratio of the Merck sub particles must have increased to that of the Merck precursor. The aspect ratio of the particles in the initial state can be roughly calculated from the platelet thickness, measurable in SEM and the $d_{50}$ of the precursors. Merck has an aspect ratio of around 8 ($d=0.3 \, \mu m, \, d_{50}=2.35 \, \mu m$) in the unprocessed state where Merck sub only has 5 ($d=0.22 \, \mu m, \, d_{50}=1.07 \, \mu m$). In parallel with the increasing aspect ratio of the particles, imperfections in the material decrease such as second phases and 2201 intergrowth.
**Influence of phase composition:** The \( J_c \) of samples processed from the unreacted precursor \( \text{Nex} 1 \) is very sensitive to the different heating rates and thus to the phase composition. At heating rates of 60 and 20°C/hr the precursor \( \text{Nex} 1 \) behaves very similarly to the fully reacted material \( \text{Nex} 3 \) and it can be expected that phase composition and particle aspect ratio are similar. Recent experiments [8] show that partially reacted precursors yield higher \( J_c \) than precursors of Bi-2212 phase composition. During heating to 850°C the \( \text{Nex} 1 \) samples react to Bi-2212. However the microstructures heated with 20°C/hr consists of larger Bi-2212 platelets and only a small amount of second phases, as indicated by the circles. In contrast, the microstructure of the precursor heated with 180°C/hr in contrast has only partially reacted and thus many small second phase particles besides fine Bi-2212 platelets are found. These findings are confirmed by the XRD measurements. All this indicates that the Bi-2212 phase formation is a key for the understanding of these results. At low heating rates \( \text{Nex} 1 \) is transformed to Bi-2212 in the same manner as \( \text{Nex} 3 \) was during calcination and thus they behave the same. At high heating rates the \( \text{Nex} 1 \) precursor finally also reacts to Bi-2212, but the aspect ratio of the particles are different and there are still many material imperfections that will act as nucleation sites for a homogeneous peritectic decomposition. Latter effect is very pronounced for the \( \text{Nex} 1 \) precursor and will be discussed in the following.

![Microstructure of pressed and polished precursors heated with 20 and 180°C/hr in the temperature range 550 to 850°C (backscatter SEM).](image)

**Figure 6:** Microstructure of pressed and polished precursors heated with 20 and 180°C/hr in the temperature range 550 to 850°C (backscatter SEM). The circles indicate nucleation sites for the peritectic decomposition and the arrows large Bi-2212 platelets of high aspect ratio.

During partial melt processing the Bi-2212 precursor peritectically decomposes to the partial melt state at around 892°C [13]. The homogeneity of this state is determined by the homogeneity of the precursor. As the peritectic decomposition is a process that has to be nucleated, only precursors with enough and homogeneously distributed nuclei can decompose uniformly. Second
phases together with the Bi-2212-2201 mixed state will nucleate the peritectic decomposition. It can be speculated that the samples heated with 180°C/hr (FIGURE 6, HR180) will yield a high temperature state consisting of second phase particles that are small and homogeneously distributed due to the higher amount of nuclei, which enables a uniform transition. The decomposition of the sample heated with 20°C/hr will start at the few nucleation sites. In FIGURE 7 the decomposition behaviour of Nexl heated with 20 and 180°C/hr is shown. The sample heated with 180°C/hr decomposed over a broader temperature range and in two steps whereas the sample heated with 20°C/hr decomposed in a narrower temperature range in a single step. This different behaviour can be attributed to the lower amount of nuclei and low melting phases like 22x1 and the mixed state. At an onset of 875°C the sample heated with 180°C/hr starts to melt around the second phases. This low temperature melting is registered by the DSC, because it is occurring extensively throughout the sample and is the consequence of a large amount of second phases (FIGURE 6, HR180). It can be expected that this low temperature melting also occurs in the sample heated with 20°C/hr but just locally very rarely. This behaviour is also expressed in the different overall energy needed for the decomposition of 30 mg of precursor which is around 2200 mJ for the sample heated with 180°C/hr in contrast to around 3000 mJ for the sample heated with 20°C/hr. The differences in decomposition energy can be explained by the less perfect material and the smaller particles of the sample heated with 180°C/hr compared to the more perfect material and large particles of the samples heated with 20°C/hr. Lower nuclei densities together with larger and more perfect grains shifts the onset of the decomposition to higher temperatures.
Figure 7: DSC measurement (10°/min in O₂) of 30 mg precursor showing the peritectic decomposition of Nex1 heated in the temperature range 550 to 850°C with 20 and 180°C/hr. The fully reacted Nex3 was used as a reference.

We see the strong influence of the particle aspect ratio and nuclei density on the ι_c of the fully processed material in the inhomogeneous peritectic decomposition of Bi-2212 to the high temperature state. Samples of fully processed precursors quenched from the temperature range in which the precursors decompose show local and inhomogeneously distributed melt formation. This is a consequence of a low number of nucleation sites for the decomposition in the sample. In this situation the aspect ratio of the particles have their influence by forming capillaries in densely packed regions where they are present as aligned platelets. Driven by the capillary forces the dense regions accumulate melt due to capillary action leaving back the peritectic phases (014x24 and 91150) without melt. These phases then cluster and remain in this clustered state, also when the whole sample has decomposed. As these clusters drastically deviate from the Bi-2212 stoichiometry they reduce the current carrying cross-section. Therefore particles of increasing aspect ratio in combination with a low nuclei density transform inhomogeneously into the partial melt state and establish an inhomogeneous microstructure in the high temperature state. These inhomogeneities can never be homogeneously equalized during further annealing.
Summarizing all the results of this work it can be stated that precursors of same stoichiometry and phase composition yield fully processed material with different $J_c$. Reasons for this can be found in the different homogeneity, particle aspect ratio and purity of the precursors, as big inhomogeneities will lead to a reduction of the current carrying cross-section and thus $J_c$ in the final product. Unfortunately both inhomogeneity, particle aspect ratio are hard to quantify or detect with standard precursor characterization methods.
1.4. Conclusions

When precursors of Bi-2212 stoichiometry peritectically decompose to the partial melt state at 892°C the nature and amounts of phases present is close to that of thermodynamic equilibrium [14]. This would indicate, that precursors of the same stoichiometry from different producers should yield similar component properties when processed identically. However, our results clearly show, that despite identical processing conditions precursors with different particle size and morphology result in components with very different \(j_c\)'s. To determine the precursor properties that determine \(j_c\), commercial Bi-2212 precursors were characterized and compared. Precursors of different particle size and phase composition, but produced by the same techniques, were processed with different heating rates during heating up to the partial melt state. Their microstructures and \(j_c\) were correlated with the properties of the precursors.

It can be concluded that the different \(j_c\) of the fully processed material can be attributed to:
(a) The different melting behaviour of the precursors, governed by precursor properties like phase composition, second phase content and stoichiometry [15], [16]. (b) Bi-2212 particle aspect ratio and nuclei density for the peritectic decomposition, having an influence on the spacial distribution of melt and solid phase particles in the high temperature state. [8]. (c) Large second phase particles like core-shell particles that assist inhomogeneous melting cannot dissolve during Bi-2212 crystallization from the partial melt state [4].

A precursor that yields material with high \(j_c\) is homogeneous, of Bi-2212 stoichiometry and can maintain its homogeneity during the peritectic decomposition. Latter criteria is the requirement for a homogeneous partial melt state with second phases homogeneously dispersed and of narrow particle size distribution and this in turn being the requirement for complete crystallization of Bi-2212 and high current carrying cross-sections.
References


Chapter 2

Influence of Precursor Inhomogeneity on the Critical Current Density of Bi-2212 Superconductors

Abstract

Particle size fractions of a commercial Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_{8+\delta}$ (Bi-2212) precursor were analysed in terms of phase composition, chemical composition, melting behaviour and morphology. These fractions reveal particle size dependent chemical compositions and consequently also different physical properties. The critical current density ($j_c$) of the partial melt processed samples of the particle size fractions varies from not superconducting to 5877 A/cm$^2$ compared to 5131 A/cm$^2$ of samples of the original and unfractioned precursor at 77 K. The most important inhomogeneities are particles of peritectic phase composition with a "core-shell" morphology which are present in the large particle size fractions. The shell consists of the Cu-free phase $\text{91150}$ and the core of Bi-free $\text{014x24}$. These core-shell particles are found to be particularly detrimental on $j_c$ as the shell induces premature inhomogeneous melting before the peritectic decomposition of Bi-2212, and the core endured the partial melt process leading to a reduced current carrying cross-section in the fully processed material. The formation of such particles could be related to inhomogeneous mixing of the initial oxide and carbonate compounds and melt formation during calcination.
2.1. Introduction

The fabrication of high temperature superconducting thick film and bulk components [1] of \(\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{8+\delta}\) (Bi-2212) is based on precursor materials in the form of Bi-2212 ceramic powders, which is partial melt processed above its peritectic decomposition temperature (895°C) and subsequently cooled slowly to crystallize Bi-2212 phase from the melt [1], [3], [4]. During heating up to 895°C in oxygen atmosphere the Bi-2212 precursors decomposes into the peritectic phases \(\text{Bi}_9\text{Sr}_1\text{Ca}_5\text{O}_{30}\) (91150), \(\text{Sr}_9\text{Ca}_5\text{Cu}_{24}\text{O}_{38}\) (014x24) and a melt. The high temperature state at 895°C of stoichiometric Bi-2212 is composed of around 40 vol% oxide melt and 40 vol% 91150 and 20 vol% 014x24 and no Bi-2212 grains. The high volume content of melt facilitates materials transport and densification. One would expect rapid homogenisation of any inhomogeneities in the material in the high temperature state. The subsequent crystallization of Bi-2212 should be independent of the precursor for a given Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry concerning its phase content, particle size, homogeneity and phase composition. However, several reports point out that the microstructure of the high temperature state (895-910°C) as well as that of fully processed Bi-2212 and its properties are strongly influenced by the precursor properties [5], [6]. Such observations are also well documented for powder in tube processed Bi-2223 [7], [8], [9] where the properties of the precursor influences microstructures and properties of the fully processed material due to the fact that the original Bi-2223 grains only partially decompose at high temperature.

So far the studies of precursor properties on the final properties of Bi-2212 have mostly focused on the influence of stoichiometry [10], [11] and different precursor preparation routes [12], [13].

Own quenching experiments during partial melt processing of a commercial stoichiometric Bi-2212 precursors shows inhomogeneous decomposition and melting behaviour near the high temperature state (880-895°C) which can be attributed to local fluctuations in the stoichiometry [10], [11], the local interaction with Ag [1], [3] and in local atmosphere variations [14]. In a later study the influence of the latter two factors were excluded, leaving stoichiometric inhomogeneity within the precursor being the only source for the inhomogeneous decomposition.

The objective of the present work is to confirm that both the strong influence of local inhomogeneity on the properties of fully processed compounds and the homogenization in the high temperature partial molten state can be attributed to the homogeneity of the precursor. The influence of precursor inhomogeneity on the properties and the final microstructures of Bi-2212
was studied in detail. In the first part of this work different particle size fractions of a precursor were characterized. The fractions were found to vary strongly in phase and chemical composition. They were partial melt processed, with their properties and microstructures evaluated. It was found that the 014x24 cores of the core-shell particles survive the partial melt state and have a deteriorating effect on the critical current density \( J_c \). These results can be explained in terms of inhomogeneity regarding the presence of the 014x24 second phase as well as the phase morphology and size. In the second part of this work particle morphology and size of the second phases on the final properties were compared. In the final part of this work the formation mechanisms of such undesired morphology of second phase particles were investigated.
Chapter 2: Influence of Precursor Inhomogeneity on the Critical Current Density of Bi-2212 Superconductors

2.2. Experimental

2.2.1. Analysis of particle size fractions of a precursor

For the study a high quality commercial precursor of Solvay (SBS) produced by the solid state route was used. The precursor was fractioned by sedimentation in a 4 m sedimentation column with methanol as a solvent. The fractions were characterized regarding particle size by X-ray diffraction centrifugation (XDC), the morphology and local particle size by scanning electron microscope (SEM), the chemical composition on a global scale by ion coupled plasma optical emission spectra (ICP-OES) and on a local scale by energy dispersive x-rays (EDX), the phase composition by x-ray diffraction (XRD) indexed with powder diffraction files (PDF) and the melting behaviour by differential thermal analysis (DTA, 10 K/min for coarse, 25 K/min for fine fractions to promote the thermal effects).

Besides the precursor analysis, samples for critical current density $j_c$ measurements were processed from the precursor fractions, using the partial melt process shown in FIGURE 1. Five samples from each precursor were made for each experiment by uniaxially pressing (250 MPa) the precursor into discs 13 mm in diameter with an initial thickness of 700 μm. The samples were processed on Ag substrates and had a final thickness between 400 - 500 μm.

![Diagram of temperature, time and atmosphere program of the partial melt process used in this study. The dashed lines indicate the quenching experiments performed in the second part of this work.](image)

Figure 1: Temperature, time and atmosphere program of the partial melt process used in this study. The dashed lines indicate the quenching experiments performed in the second part of this work.
The critical current density of the processed samples was measured with an AC-magnetometer in self field at 77 K, using the 10 μV/cm criteria ($J_c$ is about 30% higher than measured with the 1 μV/cm criteria).

### 2.2.2. Influence of second phases morphology on the critical current density of fully processed Bi-2212.

To study the influence of $0_{14x24}$ particle morphology and size in a precursor on the properties of fully processed material, 3 precursor powders were analysed and partial melt processed. The precursors are of nominal Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry and were produced by the solid state reaction route from oxides and carbonates. However their phase compositions varied strongly and the morphology and size of their $0_{14x24}$ particles, as shown in FIGURE 2. SBS is the fully reacted commercial precursor analysed in the first part of the work and has large and dense $0_{14x24}$ second phases particles present in a core-shell morphology (FIGURE 2a). The CS2 precursor is a partially reacted precursor produced by a two step calcination of Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$ and CuO, which have a purity >99.98% and typical particle size range 1 - 7 μm. With such process, the SrCO$_3$, CaCO$_3$ and CuO were first mixed in a 2:1:2 ratio and calcined at 900°C then Bi$_2$O$_3$ was mixed to the calcination product and further calcined at around 800°C. The second phase particles (FIGURE 2b) found in the final precursor are less dense with open porosity and the phases are not as separated when compared to the core-shell particles of the SBS precursor. Finally the CSC precursor was produced from the same starting materials as the CS2 precursor and is an unreacted precursor consisting of 2 compounds with one being $0_{14x24}$. Latter was produced by mixing SrCO$_3$, CaCO$_3$, and CuO in a 0.75:0.42:2 ratio and reacted at around 900°C until the precursor was single phase $0_{14x24}$. The second compound completing $0_{14x24}$ to the 2:2:1.2 stoichiometry was produced by mixing Bi$_2$O$_3$, SrCO$_3$ and CaCO$_3$ in a 2:1.25:0.58 ratio and reacted at 730°C until all the carbonates had decomposed. The resulting phase composition was Bi$_{16}$Sr$_5$Ca$_6$O$_{37}$ (16580), Bi$_8$Sr$_1$Ca$_1$O$_{14}$ (8110) and Bi$_2$Sr$_1$O$_4$ (2100). In this precursor there are no big particles, however the $0_{14x24}$ particles are dense and the phases are completely separated (FIGURE 2c). The particle size of the large second phases vary strongly, from 20 to 60 μm for the $0_{14x24}$ core of the SBS, from 3 and 7 μm for the CS2 and from 5 to 10 μm for the CSC precursor.

The phase composition of precursor SBS consisted mainly of Bi-2212 phase whereas CS2 consisted mainly of Bi-2212, 22x1 and $0_{14x24}$ phase and CSC of $0_{14x24}$ and 16580. XRD measurements of the precursors quenched during heating up to decomposition temperature show that latter 2 precursors react to Bi-2212 before they partially melt. As this study aims on the morphology of the second phases the differences in initial phase composition will be neglected.
Figure 2: Second phase particles in the precursors. (a) Core-shell assembly in precursor SBS, (b) random distribution of the phases in precursor CS2 and (c) loose and random distribution of $\text{014x24}$ in precursor CSC.

To investigate the pathway of a large second phase particle, samples of unfractioned SBS precursor were quenched at different stages of the partial melt process (FIGURE 1). At the target temperature the samples were quenched into oil. The quenched samples were polished and analysed by SEM focusing on the evolution of the microstructure.

2.2.3. Formation mechanism of large second phase particles

To study the formation mechanism of the large second phase particles of core-shell morphology found in the SBS precursor a Bi-2212 precursor was produced in-house from high purity oxides and carbonates as specified in the previous section. The precursor was made by the same 2 step process used for the CS2 precursor but using a higher temperature for the second calcination. After the first calcination step, XRD studies reveal a phase composition of Sr$_{1.5}$Ca$_2$CuO$_3$ (01x1), Sr$_2$Ca$_2$CuO$_3$ (02x1) and some unreacted SrCO$_3$. By performing the second calcination of the nominal Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry at 840°C after adding Bi$_2$O$_3$ to the first calcination product sufficient melt was formed. Bi$_2$O$_3$ forms a low eutectic melt with small amounts of CuO at around 771°C in air and has excellent wetting behaviour which allows it to readily spreads through the SrCaCu oxide precursor. Furthermore the effect of annealing time was examined for 50 and 200 hrs. The resulting precursor powders were characterized by SEM micrographs and samples were processed.
2.3. Results and Discussion

2.3.1. Analysis of particle size fractions of a precursor

The particle size distribution of the SBS precursor is shown in FIGURE 3. The \( d_{50} \) value is at 9 \( \mu \text{m} \) and particles as large as 55 \( \mu \text{m} \) were found. Furthermore, the microstructures confirm that these large particles are not agglomerates of Bi-2212 but "core-shell" particles with a porous 014x24 core and a rather dense 91150 shell as shown in the inset of FIGURE 3.

![Particle size distribution](image)

Figure 3: Particle size distribution of the precursor produced by the solid state route. Insert: Characteristic particle of the larger precursor particle fractions.

The physical and chemical properties of the SBS precursor fractions and processed samples of the fractions are presented in FIGURE 4 and FIGURE 5. In FIGURE 4a the phase composition of fractions are shown. Large particle size fractions consist mainly of 014x24 and 91150 whereas the fine fractions of the SBS precursor have almost no 014x24. The broadening of the Bi-2212 XRD peaks in the fine fractions indicates that a Bi-2212-2201 solid solution is present (Bi-2212 with 2201 intergrowths). Here, it should be noted that due to the core - shell morphology of the particles, the XRD phase analysis emphasizes the 91150 shell and not the 014x24 core. The DTA results of the respective particle fractions are shown in FIGURE 4b, where the first peak (T<900°C) is assigned to the peritectic decomposition of Bi-2212 to 014x24, 91150 and a melt.
The melting behaviour of the different fractions is distinctively different and the shift to lower melting temperatures with decreasing particle size is due to the increasing amount of 2201 intergrowths in the Bi-2212 grains. The second peak (T>900°C) is the transformation of 014x24 to 01x1 which persist to high temperatures in equilibrium with the melt [16]. The temperature at which the first melt is formed is plotted in FIGURE 5b, where it can be seen that the fractions decompose over a temperature range of 40°C confirming the inhomogeneous melting of the SBS precursor and also observed by several authors [17], [18], [19] in other Bi-2212 precursors.
Figure 5: SBS precursor properties in dependence of its particle size fractions: (a) Chemical composition, (b) melting temperature and (c) critical current density, $J_c$, ($10 \mu V/cm$, 77 K in self-field) of the fractions showing strongly particle size dependent properties. The grey horizontal lines in the figures correspond to the properties of the unfractioned precursor.
As evident from FIGURE 5a the chemical compositions of the fractions vary with particle size i.e. large particles are richer in Cu and Ca than the overall Bi-2212 stoichiometry, whilst small particles, are deficient in Ca and enriched in Bi. In FIGURE 5c, the critical current densities $J_c$ are shown. As expected the $J_c$ of the processed fractions vary substantially. $J_c$ is low for samples made of small (< 4 μm) and large (>20 μm) particle fractions and shows maximum values for fractions with a particle size between 5 and 15 μm. This correlates with the chemical composition. Maximum $J_c$ appears at Bi:2, Sr:2, Ca:1, Cu:2 stoichiometric composition and deviations from this stoichiometry lead to a rapid drop in $J_c$. The fact that the fractions with particle sizes between 5 and 15 μm, which makes around 70 wt% of the unfractioned precursor, have a $J_c$ higher than the $J_c$ of the unfractioned precursor, indicates that the remaining fractions are very detrimental. This can either be due to the composition and/or the morphology of these fractions. To fully understand the strong $J_c$ dependence of the samples microstructure analysis in needed.

In FIGURE 6 the microstructures of the fully processed samples from the different particle size fractions of the SBS precursor are shown. The microstructures of material made of the large particle size fractions, consisting mainly of core-shell particles, are full of initial and unreacted cores embedded in a matrix of Bi-2212 (FIGURE 6a,b). Comparing FIGURE 6a with FIGURE 6b the influence of the core-shell particles becomes obvious. The precursor with high fractions of core-shell particles results in partial melt processed material with a high area fraction of dark phase, corresponding to 014x24. Much less of latter phase is present in the microstructure of the material presented in FIGURE 6b, produced from a precursor fraction with less and smaller core-shell particles. The $J_c$ of these two examples were 100 and 2000 A/cm² indicating the detrimental influence of 014x24 in the precursor as well as in the final microstructure on the superconducting current carrying capacity. On the other hand samples made of finer precursor fractions which were free from 014x24 core-shell particles resulted in very homogeneous microstructures that were nearly free of residual 014x24 phase as presented in FIGURE 6c and FIGURE 6d. However the decreasing $J_c$ and finally complete loss of the superconducting properties at 77 K of samples processed from very fine precursor fractions can be explained by the increasing amounts of 2201 intergrowths that form as a consequence of off-stoichiometry, seen as bright stripes within the Bi-2212 bands in the microstructures.
Chapter 2: Influence of Precursor Inhomogeneity on the Critical Current Density of Bi-2212 Superconductors

Figure 6: Microstructures of processed material of the particle size fractions. The matrix is Bi-2212, the dark phase is 014x24 and the bright is 2201. (a) The large cores of the core-shell particles are embedded in Bi-2212. (b) In the Bi-2212 matrix there are smaller cores of the core-shell particles. (c) Plain Bi-2212 matrix with no more initial second phase. (d) Large amounts of 2201 intergrowths in Bi-2212 visible as bright stripes within the matrix.

It is somewhat surprising that the core of the core-shell particles survive the partial melt process which can be clearly seen in FIGURE 7. Compared to the initial particles shown in FIGURE 3 and FIGURE 9 only the Bi-rich shells dissolves during the partial melt process. Due to their phase composition (014x24), corresponding to the Bi-free peritectic phase, the cores will grow in the high temperature state and only get partially dissolved during crystallization of Bi-2212 due to slow kinetics.
Chapter 2: Influence of Precursor Inhomogeneity on the Critical Current Density of Bi-2212 Superconductors

Figure 7: Cores of the initial core-shell particles after processing, (a) made of fraction with a \(d_{50}=56\ \mu\text{m}\), (b) made of fraction with a \(d_{50}=37\ \mu\text{m}\). No dissolution of the core during the partial melt state.

Summarizing the different results of samples processed from different size fractions of the SBS precursor, the following picture emerges: Fractions of different particle size have different chemical composition and therefore different phase compositions, consequently they show different melting behaviour and different final \(J_c\). The melting/decomposition temperature of the different powder fractions decreases with decreasing particle size due to change in chemical composition (Bi-rich and Ca deficient). Large second phase particles show a core-shell microstructure. The core consisting of porous \(014x24\) and the shell of a rather dense Bi-rich phase \((91150)\). These particles survive the partial melt process and substantially reduce the current carrying cross-section. The stoichiometry, melting temperatures as well as phase composition of fractions with particle sizes <3.5 \(\mu\text{m}\) indicate increasing amounts of the one layer compound 2201 in Bi-2212 grains.

The previous results show the harmful effect of core-shell particles on \(J_c\). As only the cores of \(014x24\) survive the partial melt state the limiting effect on \(J_c\) can be attributed to this phase and its morphology.

2.3.2. Influence of second phases morphology on the critical current density of fully processed Bi-2212.

The analysis of the different particle size fractions of the SBS precursor presented in the previous section showed that nearly all of the fractions, except the very fine, had some \(014x24\) second phase impurities. However, they differed in quantity, particle size and morphology, and the critical current density \(J_c\) thereof also differed strongly. We now want to elucidate further the
influence of the $0_{1}4_{x}2_{4}$ particle morphology on the $J_c$ of fully processed material. Therefore two additional precursors with explicitly different $0_{1}4_{x}2_{4}$ second phases contents and morphology to the initially analysed $SBS$ were produced, analysed and processed.

The $J_c$ of identically partial melt processed material ranges from 5131 A/cm$^2$ for the $SBS$, 7060 A/cm$^2$ for the CS2 and 6790 A/cm$^2$ for the CSC precursor. $J_c$ seems to correlate with the particle size of the large second phases. This result clearly indicates that it is not the $0_{1}4_{x}2_{4}$ phase that is responsible for the low $J_c$, but rather its morphology.

To clarify the detrimental influence of the core-shell morphology on $J_c$, samples of the unfractioned $SBS$ precursor were quenched from different processing temperatures. The microstructures are shown in FIGURE 8. With increasing temperature the Bi-2212 grains and the core-shell particles start to sinter together (FIGURE 8b). At temperatures close to the peritectic decomposition temperature of Bi-2212 (FIGURE 8c), local melting zones are formed around the core-shell particles as the shell melts. Finally in the partial melt state the $0_{1}4_{x}2_{4}$ cores are preserved due to its phase composition and its size (FIGURE 8d).
The experiments show that core-shell particles have a negative influence on $J_c$ in several manners: (a) The accumulation of Sr, Ca and Cu in these particles has severe consequences on the stoichiometry of the rest of the material and thus on the superconducting properties. Bi-rich Bi-2212 melts at lower temperatures giving the second phases more time to grow. During crystallization of Bi-2212 from the melt the large second phases will sterically hinder the formation of a percolating Bi-2212 network of platelet grains and by accumulating Cu and Ca, the two elements needed to intercalate 2201 into Bi-2212. (b) The formation of local melting zones before the peritectic decomposition reduces the homogeneity of the material by forming regions of high
density which are Bi-rich and by letting second phases locally grow. It can be speculated that the wide particle size distribution of the peritectic phases in the high temperature state origin from this inhomogeneous melting.

Summarizing the results, it can be stated that peritectic second phases \(0_{14x24}\) (core) and \(9_{1150}\) (shell) are only undesired as large particles, clusters or core-shell particles. Therefore they have to be avoided during precursor production.

### 2.3.3. Formation mechanism of large second phase particles

To study the formation of core-shell particles several calcination experiments were performed. Particles of core-shell morphology have not been found in precursors produced from an initial starting composition of Bi:2, Sr:2, Ca:1, Cu:2 of carbonates and oxides, although large \(0_{14x24}\) second phase particles have also been found. Model experiments with agglomerates of starting powders in the initial oxide and carbonate mixture and melt formation during calcination have been performed showing maintenance or even promotion of the inhomogeneity but no core-shell particle formation. Thus the studied precursor had to be produced by another production route. A possibility is that in first the cores were produced and then were encapsulated by a melt as described in the experimental part of this section.

Core-shell were found in the precursors produced by the two step calcination and dependent on the annealing time at \(840^\circ\text{C}\). The latter influences the morphologies of these grains, as shown in FIGURE 9. A densification of the core takes place closing the initially open porosity. The quantification of the micrographs exhibits that the phase contents in average stays the same, 57% \(0_{14x24}\) core and 43% \(9_{1150}\) shell independent of the annealing time, however the porosity decreases from 17% after 50 hrs. at \(840^\circ\text{C}\) to 7% after 200 hrs. at the same temperature. The chemical composition of the core and shell phases also stays the same as EDX measurements show. The core-shell particles all have a size larger than 30 \(\mu\text{m}\) indicating a minimal size for their formation. It is expected that the smaller particles rapidly react with the melt and form the Bi-2212 phase. In parallel to the densification of the core-shell particles in the precursor a decay of \(J_c\) in the fully processed material thereof has been found. \(J_c\) of the precursor annealed for 200 hrs. is 24% lower than of the precursor annealed for 50 hrs.
In FIGURE 10 a formation mechanism of the core-shell particles is proposed. The calcined CaCO₃, SrCO₃ and CuO precursor of the first step was completed with Bi₂O₃ to a nominal composition of Bi-2212. This powder contains some agglomerates of unreacted oxides and carbonates (FIGURE 10a). During the consequent heat treatment, the added Bi₂O₃ melts and encapsulates the agglomerates. The very wetting melt creeps inside the agglomerates and decomposes the carbonates releasing CO₂. This gas prevents massive penetration of the Bi₂O₃ melt and also prevents it from solidification. A CO₂ rich atmosphere decreases the melting temperature of Bi₂O₃ to around 740°C (FIGURE 10b). After the complete carbonate decomposition in the agglomerates, a rigid network of pores and SrCaCu oxides are left. In parallel a depletion of Sr and Ca from the core takes place, leading to the 91150 phase formation in the shell and the consequent solidification. The phase composition of the core is now 014x24. Assisted by some residual melt in
the grain boundaries of the core, sintering now takes place densifying the core. After the densification this melt is found in the triple grain boundaries and the residual CO$_2$ in the now closed pores.

![Diagram of core-shell particles](image)

Figure 10: Formation mechanism of core-shell particles. (a) Mix of the incomplete calcined Sr Ca Cu carbonates and oxides with Bi$_2$O$_3$, (b) heating up and beginning of the calcination and (c) after the annealing.

Core-shell particles are the result of inhomogeneous mixing, incomplete calcination and improper calcination parameters. Agglomerates of SrCaCu carbonates and oxides get encapsulated by a Bi-rich melt that forms at temperatures below the Bi-2212 phase formation temperature (800°C).
2.4. Conclusions

In this work the homogeneity of a commercial precursor produced by the solid state route was analysed. The particle size fractions have different phase compositions, morphologies and melting behaviour. Partial melt processed samples show different \( J_c \), which can be attributed to the different chemical compositions of the fractions. Finer fractions of the precursor are Bi-rich and Ca-poor leading to lower melting temperatures and large amounts of 2201 intergrowths in fully processed material were detected, correlating with the diminishing \( J_c \). Coarse fractions have particles with core-shell morphology with a 014x24 core and a Bi-rich shell. During partial melt processing the shells melt at lower temperatures, creating inhomogeneous melting and the cores survive the partial melt state due to their size and phase composition. The cores interrupt the formation of a percolating Bi-2212 network and reduce the current carrying cross-section.

The presence of second phase particles in the precursor Bi-2212 powder is not detrimental as long as they are small in size and uniformly distributed. However, if they are large in size and well sintered, e.g. core-shell particles, \( J_c \) will be adversely affected.

The formation condition of the core-shell particles was demonstrated through a two step calcination route where Bi\(_2\)O\(_3\) is only added after the second calcination step. If the second calcination is carried out at excessive temperatures, a low melting Bi-rich melt is formed and it encapsulates agglomerates containing unreacted carbonates of the first calcination step. Furthermore, the initial loose core-shell particles could sinter to dense particles with a 014x24 core and a 91150 shell.

The critical current density \( J_c \) of fully processed material is strongly determined by the chemical homogeneity and the phase composition of the precursor. Especially, phase inhomogeneity present in the precursor powder, e.g. core-shell particles may not be homogenized in the partial melt state and instead may be preserved to the final microstructure, both leading to a reduction in the effective current carrying cross-section. Therefore the production of high \( J_c \) Bi-2212 material requires precursors that are homogeneous.
Chapter 2: Influence of Precursor Inhomogeneity on the Critical Current Density of Bi-2212 Superconductors

References


Chapter 2: Influence of Precursor Inhomogeneity on the Critical Current Density of Bi-2212 Superconductors
Chapter 3

Influence of Precursor Calcination Parameters on the Critical Current Density of Bi-2212 Superconductors

Abstract

Partial melt processed $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{8+\delta}$ (Bi-2212) materials have low critical current densities ($J_c$) when made from precursors where melting occurred during the calcination. In this paper the origin of melt formation during calcination of a stoichiometric Bi:2, Sr:2, Ca:1, Cu:2 mixture of oxides and carbonates was identified and the consequences of this melt on the homogeneity of the calcination product and of fully processed Bi-2212 material studied. It was found that low oxygen partial pressure ($pO_2$) atmospheres can build up inside the precursor particle network during the decomposition of the carbonates. This causes melt formation below 750°C during calcination leading to phase separation and inhomogeneities in the calcined powder. The consequences of these inhomogeneities in the precursor on the $J_c$ of fully processed material and their microstructures was studied. In order to prevent melting below the peritectic decomposition temperature in the green bodies the calcined precursors should be carbonate free but not yet fully converted to Bi-2212 in order to obtain maximum $J_c$ in partial melt processed material. A calcined precursor that yields components of high $J_c$ shows maximal homogeneity on short length scales (<10 µm) just before it peritectically decomposes.
3.1. Introduction

For the production of high temperature superconducting bulk material [1] such as Bi-2212 the classical ceramic processing route - precursor synthesis, shaping and firing is the choice of preparation route. As in classical ceramics, the precursors have a strong influence on the microstructure and the properties of the final product. (A precursor is a powder from which HTSC compounds are processed.)

The preparation of high temperature superconductor precursors can be divided into 3 major processing steps: Selection of starting materials, mixing and calcination. For Bi-2212, many different starting materials like oxides and carbonates [2][3][15], hydroxides [8][13], nitrates [4][5][6][11][12] and metals [9] are described. Different mixing techniques like the citrate route [2], solid state route [3][13], “melt quenching” [15], precipitation routes [4][6], spray pyrolysis [5], freeze drying [12], electrostatic deposition route [8][11] have been applied. The high diversity of applied starting compounds and mixing routes have the common goal to get a reactive and homogeneous mixture of the starting elements. Only then homogeneous Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_{8+d}$ (Bi-2212) precursors that yield Bi-2212 components with high critical current densities ($J_c$) can be produced. Each production route has its benefits and drawbacks. The major challenges are the control of the stoichiometry, preservation of homogeneity during the entire process, prevention of contamination and the purification of processing agents. The final step, the calcination, is bound to a heat treatment usually done in several steps, using different temperatures ranging from 750 [5] to 860°C [3][9], and annealing times from minutes [5] to days [13]. Most of the calcination parameters are determined by the reactivity of the initial starting materials. However independent of the starting materials chosen, a heat treatment in air in excess of 800°C is needed in order to get the Bi-2212 phase.

The influence of the precursor production route on the final properties of processed Bi-2212 components has been systematically studied by several groups as listed in TABLE 1. As starting materials oxides and carbonates (Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$, CuO) or acetates (Bi(CH$_3$COO)$_3$, Sr, Ca, Cu(CH$_3$COO)$_2$ were used. They were mixed and stabilized by different techniques, like co-precipitation, sol-gel, melt quenching, spray pyrolysis or the solid sate reaction.

In the co-precipitation technique the ions are precipitated together from a sol by addition of an agent initiating the formation of an insoluble molecule, like carbonates, oxalates, acetates and citrates. The sol-gel route also starts with a sol which is then transformed to a gel by changing...
In the spray pyrolysis technique the sol is sprayed into a furnace in which the solvent is burned and the metal ions react with each other and oxygen to oxide phases. In the melt-quench technique the starting compounds are molten at high temperatures and then quenched. Finally in the solid state reaction route the starting compounds react by solid state diffusion to the desired phases. It follows from the previous works listed in TABLE 1: $J_c$ varies in dependence of the precursor production route around ±500 A/cm² and of the processing route to the Bi-2212 component around ±1000 A/cm². $T_c$ of a precursor material cannot be correlated with the $J_c$ of the processed material. Therefore $J_c$ is determined by both, the precursor properties, and the process to the Bi-2212 compound.

The $J_c$ of partial melt processed Bi-2212 is very sensitive to the current carrying cross-section, which is determined by the amount, size and distribution of residual second phases in the microstructure. It has been shown that latter is dependent on both, the processing parameters such as heating rates, annealing times, atmospheres and maximum temperature [20][21] and on precursor inhomogeneities, like large second phase particles [19]. Optimized processing parameters to process a green body to a Bi-2212 component can however only yield high $J_c$ material with homogeneous precursors in which homogeneity can be preserved through all the processing steps to the fully processed material - independent of the production route and process.

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Table 1: Overview of the Bi-2212 precursor production routes and the properties of material processed therefrom. SF...Sinter forged, PMP...partial melt processed, LFZ...Laser floating zone.
The solid state approach is the most often used for Bi-2212 precursor synthesis, because of its simplicity. In all the previous works the starting materials reacted to oxides and carbonates after decomposition of the organic ligands below 350°C upon heating in air. Therefore, the reaction pathways to Bi-2212 are similar, while the formation rates vary, depending on which starting compounds are chosen. During calcination of the starting materials, after burnout or decomposition of the carbonates, the 2201 phase starts to form around 600°C. At 700°C the first Bi-2212 starts to form, however only above 800°C it rapidly forms at the expense of 2201 due to intercalation [14], [17]. The reaction rates can be accelerated using reactive, high surface area starting material or by the calcination parameters such as temperature, heating rate and oxygen partial pressure in the atmosphere. However no systematic study is known to correlate the final microstructure of Bi-2212 and the critical properties ($T_c$ and $j_c$) with processing parameters of the starting components and the resulting Bi-2212 microstructures obtained after processing the Bi-2212 precursors.

In a recent study of the authors [19] it was found that the homogeneity of a precursor is one of the most important issues to achieve Bi-2212 components with high $j_c$. Thereby it was found that the undesired formation of melt during calcination can strongly reduce the homogeneity of a precursor and result in fully processed components with low $j_c$. This melt reduces the homogeneity on a large length scale (around 200 μm) by promoting undesired phases, enabling grain growth and encapsulating large unreacted particles which themselves then form local equilibrium. Therefore it was concluded, that melt formation with phase separation during calcination is detrimental to the homogeneity of the calcination product.

The aim of this work is to correlate the precursor calcination pathway with the occurrence of melt and phase separation in the calcined product and to identify those conditions leading to homogeneous calcination products for high $j_c$ partial melt processed Bi-2212. We characterized the calcination process in oxygen and CO$_2$ of oxide and carbonate powder mixtures by DSC and TG for different heating rates. Carbonate decomposition produces low oxygen partial pressures in the precursor leading to rather low melting temperatures of 750°C, specially under high heating rates. This melt led to phase separation in the calcined product which adversely influence $j_c$ in partial melt processed Bi-2212. In case excess melt formation and grain coarsening is avoided during calcination, more homogeneous calcination products can be obtained leading to high $j_c$ after partial melt processing.
3.2. Experimental

3.2.1. Precursor preparation parameters

As starting powders, Bi₂O₃, SrCO₃, CaCO₃ and CuO, which have a purity of >99.98% and typical particle size range of 1 - 7 μm were used in this study.

The starting compounds were mixed in parts to get Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry and ball milled in butylacetat (Fluka, purum) as a solvent with 1-2 wt% Span 80 (Fluka) as a dispersion agent. After gentle ball milling in plastic jars with ZrO₂ balls for 2 days, the solvent was slowly evaporated while milling to avoid sedimentation. The dispersion agent was slowly burnt out in a large glass container at 350°C for 24 hrs. No Zr impurities were detected by EDX in the final dry mixture. This unreacted mixture of oxides and carbonates is, denoted "starting material" in this work.

Differential scanning calorimetry (DSC) and thermal gravimetry (TG), (Netzsch STA449C Jupiter) was performed on 50 mg of starting material. The loose or isostatically pressed powder samples were heated in Al₂O₃ crucibles with a heating rate of 180°C/hr to 550°C, then with 180 and 900°C/hr to 850°C where they were annealed for 1 hr. The experiments were performed in oxygen and CO₂ atmosphere. Binary (Bi₂O₃-CaCO₃ and Bi₂O₃-CuO) and ternary (Bi₂O₃-CaCO₃-CuO) mixtures were also measured under CO₂ atmosphere.

Calcination experiments were performed in silver trays. The starting material was loosely spread in batches of 15 - 20 g in Ag trays. The packing height varied between 10 - 20 mm corresponding to a packing density of 1 g/cm³. After calcination the precursors were milled in an achat mortar and pistil by hand and sieved (63μm). The following calcination parameters were varied: Heating rate to the calcination temperature, calcination atmosphere, the packing density of the starting material during calcination, calcination-temperature and time. The parameter ranges are listed in TABLE 2. All uncalcined mixtures were first heated to 550°C with a heating rate of 180°C/hr and thereafter according to the experimental parameters listed.
Chapter 3: Influence of Precursor Calcination Parameters on the Critical Current Density of Bi-2212 Superconductors

<table>
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<td>12</td>
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Table 2: Parameters of the calcination experiments.

The reference precursor used in this work is a high quality commercial precursor supplied by Solvay.

3.2.2. Calcination with reduced atmosphere exchange

During this work it was observed that a CO₂ rich atmosphere during calcination of the starting material can be the source of melt formation, despite a general air atmosphere in the furnace. To study the conditions under which such a CO₂ rich atmosphere can form in the particle network during calcination and to study its consequences on the homogeneity of the precursor, calcination was done in a setup where atmosphere exchange between the powder batch and the furnace atmosphere is insufficient. Therefore a 10 cm high hollow cylinder of Al₂O₃ with a diameter of 1cm was placed vertically on an Al₂O₃ plate and filled with the starting material. The setup was heated with a heating rate of 60°/hr to 820°C and annealed for 48 hrs in an air flushed furnace. After calcination the solid sample was cut in sections and analysed by SEM.

3.2.3. Partial melt processing of the calcined precursors

The sample processing and partial melt process were the same for all precursors obtained according to Table 2. Five samples of each precursor were made for each experiment by uniaxially pressing (250 MPa) the precursor into pellets and processed on Ag substrate according to the sequence shown in Figure 1. The sample dimensions were 13 mm in diameter with an initial thickness of 700 μm and a final thickness of around 400 - 500 μm after partial melt processing.
Figure 1: Temperature, time and atmosphere program of the partial melt process used in this study.

The critical current density $J_c$ of the processed samples was measured with an AC-magnetometer, using the 10 μV/cm criteria ($J_c$ is about 30% higher than measured with the 1 μV/cm criteria). The microstructures and phase compositions of the precursors and fully processed samples were characterized by SEM and XRD (Cu Kα).
3.3. Results

3.3.1. Calcination conditions that lead to melt formation

DSC and TG measurements with the unreacted starting material were done in the temperature range of 550 to 850°C. In Figure 2 the DSC signals and weight loss of loose and isostatically pressed starting material heated with 180 and 900°C/hr in an O₂ and a CO₂ atmosphere are shown.

The loose samples heated with 180 and 900°C/hr in an oxygen atmosphere show 4 reaction peaks and an increase of enthalpy during heating up. This increase of enthalpy starts after the first reaction peak and corresponds to phase formation processes. For moderate heating rates of 180°C/hr the first peak has an onset of 640°C and the others have merged to a rather weak but broad peak which has an onset around 771°C. The peaks represent the decomposition of CaCO₃ (CaCO₃ to CaO equals to a mass loss of 4.25%) first and later SrCO₃ (SrCO₃ to SrO equals to a mass loss of 8.5%)—as indicated by the mass loss (TG). At high heating rates the peaks are much more distinct and larger and are shifted to higher temperatures. The onset of the first decomposition peak is shifted from 640°C to 670°C and the other peaks have onset temperatures around 771°C, 798°C and 830°C. The results are in good agreement with the weight loss of the reacting precursor. At high heating rates the weight loss in the temperature range 550 to 850°C is less than for moderate heating rates, indicating that at high heating rates there are still carbonates present in the precursor even at 850°C.

After the measurements the samples were still powder products, however the sample heated with 900°C/hr consisted of large and hard agglomerates. The latter is an indication that melt was formed only in very small amounts. In the Bi-Sr-Ca-Cu-O system the lowest eutectic oxide melt is found at 771°C in oxygen and has a composition of Bi₀.903Sr₀.032Ca₀.015Cu₀.05O₁.₄₅ according to calculations with ThermoCalc using the database assessed using the CALPHAD approach [18]. This temperature of 771°C corresponds to the second peak. The occurrence of melt is the reason for the formation of hard agglomerates. The intensity of this peak increases with higher heating rates as did the formation of hard agglomerates.

Phase diagram calculations show [18] that the melting temperatures of oxide liquids are lowered with decreasing pO₂ in this system. Therefore, the rapid decomposition of carbonates forming a low pO₂ atmosphere in the powder sample results in the formation of melt already at low
temperatures. To reduce the gas exchange of the sample with the furnace atmosphere, starting material was isostatically pressed (30 MPa) and then calcined with a heating rate of 180°C/hr in oxygen. The DSC result differs from the result of the loose starting material heated under the same conditions, however the TG results are very similar (FIGURE 2). The overall enthalpy of the sample is on average higher than of the loosely packed samples and two broad peaks are present. The onset of the first peak is at 675°C and corresponds to the carbonate decomposition and the onset of the second peak is at 807°C and possibly corresponding to melt formation. After the measurement the sample was very hard and had to be broken up, suggesting melt assisted sintering.

The same behaviour can be obtained when annealing under CO2 atmosphere instead of oxygen. The occurrence of a melt was obvious as the sample had undergone strong volume shrinkage laterally and was completely solid after this annealing. However, already small amounts of melt were sufficient as it did not flow away. The DSC result shows 3 peaks, the first is small and blurred with an onset around 660°C which is followed by the main peak with an onset of 743°C and finally a third small peak with an onset of 807°C (FIGURE 2). A first minor weight loss is found around 650°C which is followed by a weight gain, before a strong weight loss was registered during the second DSC peak. To understand this result, and especially the melt formation, the experiments with binary and ternary mixtures were performed in CO2 and Ar atmosphere. The atmosphere was changed to investigate if the melt that forms is of oxide or carbonate nature. The results show that oxide melts are formed and CO2 only reduces the pO2. At a pO2 of 10⁻².¹⁵ bar the melting temperature of Bi₂O₃-CuO is reduced from 792°C to 739°C by the presence of CaO. The decomposition of CaCO₃ starts at around 660°C only with the presence of Bi₂O₃ in a CO2 atmosphere. Therefore the first weak peak in the measurement with starting material in a CO2 atmosphere is a first decomposition of CaCO₃. The CaO then enables the formation of the eutectic melt as indicated by the second peak, which is 28°C lower due to the low pO2 compared to the eutectic in oxygen at 771°C. This shift to lower temperatures is a consequence of low pO2 and could be confirmed by thermodynamic calculations [18]. The third peak corresponds to partial SrCO₃ decomposition.
Figure 2: DSC and TG measurements were performed with the loosely packed and pressed starting material in the temperature range 550-850°C. The heating rates applied were 180 and 900°C/hr in O₂ and CO₂ atmosphere.

As expected, the DSC and TG results differ strongly in dependence of the atmosphere and the heating rate. At high heating rates the temperature at which all CaCO₃ has decomposed is around 30°C higher compared to moderate rates of 180°C/hr. In a CO₂ atmosphere only CaCO₃ decomposes and the temperature at which all has decomposed is around 150°C higher than in a non CO₂ atmosphere (O₂, Ar). The results of the pressed sample heated with 180°C/hr in O₂
indicate behaviour similar to the results of the sample heated with high heating rates and with increasing temperature to the results of the sample heated in CO$_2$ atmosphere. The temperature at which all CaCO$_3$ has decomposed is around 10°C higher than for loose powder and the broad peak with an onset of 807°C corresponds to the third peak of the sample heated in CO$_2$.

Low p$_{O_2}$ in the powder sample can be generated by high heating rates liberating a large fraction of the CO$_2$ in a short time period or by hindered gas exchange with air of the furnace environment. Consequently melt is formed leading to inhomogeneities in the precursor. High p$_{O_2}$ and moderate heating rates, together with a permanent good gas exchange in the powdery sample, allows the complete decomposition of the CaCO$_3$ below 700°C and SrCO$_3$ below 850°C. The phase formation then occurs without liquid being formed and therefore the initial homogeneity of the fine powder in the calcined product is preserved.

3.3.2. Calcination with reduced gas exchange

Calcination of starting material at reduced p$_{O_2}$ will lead to the formation of melt. To illustrate that low p$_{O_2}$ can be generated in a reacting oxide and carbonate powder mixture, starting material was calcined (60°/hr to 820°C, 48 hrs. annealing) in a set up where exchange of gas is only marginally possible. Our hypothesis is that CO$_2$ gas from the carbonate decomposition is locally trapped inside the particle network of starting material due to insufficient gas exchange. The melting temperature of the starting material should then be decreased to 740°C at low p$_{O_2}$ (10$^{-2.15}$ bar) as the DSC/TG experiments have shown. The resulting local melt then rapidly decomposes further carbonates keeping the CO$_2$ partial pressure sufficiently high (and the p$_{O_2}$ low) to enable further melt formation. The specimen preparation and set up was chosen as described in 3.2.2.

The precursor obtained after the calcination was a solid cylinder of 0.5 cm diameter and 8 cm height, corresponding to a shrinkage in volume of 80%. The microstructure was very inhomogeneous as shown in FIGURE 3, independently of the position in the cylinder. Different regions can be distinguished in the microstructures: (a) Regions of high SrO and CuO particles concentration with mixed state (Bi-2212-2201) in-between, (b) a ring of 2201 (bright phase) with no SrO and CuO particles inside surrounding the, (c) pores. The surprising dense microstructure together with the large scale separation of phases are due to the occurrence of considerable amounts of melt in the precursor during calcination.
Figure 3: Microstructure of the precursor calcined in a cylinder with hindered gas (air) exchange with a heating rate 60°/hr to 820°C and annealed for 48 hrs. (a) Large pores were formed due to entrapped CO₂ from decomposing CaCO₃. (b) CuO, SrO and 22x1 phases are separated due to the occurrence of low temperature (750°C) melt during calcination. (c) Large grains of 22x1 are precipitated from the melt leading to phase separation on the length scale of 100μm.

This experiment clearly shows that the melt formation during calcination is a consequence of insufficient gas exchange. CO₂ originating from the CaCO₃ decomposition enables a Bi-rich melt to form at temperatures as low as 740°C. This reactive melt then initiates further carbonate decomposition producing more CO₂ gas (FIGURE 3b). When spreading melt fronts from different directions meet, the CO₂ gas gets entrapped and large pores are formed (FIGURE 3c). Finally the melt solidifies to Bi-2212 and 22x1, depending on the elements available locally. These results clearly show that melt formation during calcination promotes the formation of inhomogeneities on a length scale of 1000 μm.
3.3.3. Influence of heating rate during calcination

In order to illuminate the role of inhomogeneities formed during calcination on the critical current density, the starting material was heated up to the calcination temperature of 850°C in air at different heating rates and annealed for different lengths of time. Precursor inhomogeneities fostered by melt are large 2201 and Bi-2212 particles with high aspect ratios and coarse second phase particles.

The properties of the precursor properties strongly differed in dependence of the heating rate and the annealing time. The precursors heated at 900°C/hr to 850°C were hard and the particles stuck together in large agglomerates, indicating the presence of a melt during calcination. On the other hand the precursors produced by 20 or 180°/hr were fine and soft powders.

The $J_c$ of fully processed material of the precursors produced by different heating rates between 550°C and 850°C are shown in Figure 4. High $J_c$ were obtained when applying slow heating ramps during calcination. Too high heating rates resulted in low $J_c$. In the temperature range 800°C to 850°C, on the other hand, the heating rate did not influence $J_c$.

Higher $J_c$ were achieved for all the samples processed from precursors annealed for 1 hr at 850°C rather than 12 hrs.
Chapter 3: Influence of Precursor Calcination Parameters on the Critical Current Density of Bi-2212 Superconductors

Figure 4: Influence of the heating rate during the calcination of the initial oxide and carbonate mixture on the $j_c$ of the fully processed material. The full line corresponds to heating rates between 550 and 850°C, the dashed lines to those between 800 and 850°C. At the calcination temperature of 850°C the samples were annealed for 1 hr (upper data points) and 12 hrs. (lower data points).

The microstructures of the precursors are shown in FIGURE 5. With increasing heating rate a coarsening of the microstructures takes place (FIGURE 5a, b, c), which is amplified by prolonged annealing (FIGURE 5c, d, e). Although the average size of the SrO and CuO particles remain the same, their distribution changes from homogeneously distributed single grains to large agglomerates that are inhomogeneously distributed. With increasing heating rate the morphology of the layered compounds 2201 and Bi-2212 changes from small almost isotropic grains to large and strongly anisotropic ribbons.

XRD analysis shows different phase compositions resulting from the different reaction pathways, also reflected by the microstructures. The main results from the phase analysis show that 22x1 phases of different stoichiometries are formed in dependence of the heating rate, which then react at different rates to Bi-2212. For high heating rates 22x1 with $x=0.4$ is formed, corresponding
in stoichiometry to the composition of the peritectic melt present in the high temperature state. For low heating rates on the other hand the Ca free compound 2201 is formed. The phase composition of the annealed precursors shows that 22x1 reacts more rapidly to Bi-2212 than Ca free 2201.

Figure 5: Microstructures of precursors heated to 850°C with heating rates of, (a) and (d) 20 °C/hr, (b) and (e) 180°C/hr, (c) and (f) 900°C/hr and annealed for (a),(b) and (c) 1 hr and (d), (e) and (f) 12 hrs. Homogeneous microstructures (a) and (b) are obtained for low heating rates and short annealing times.

The microstructures indicate that the homogeneity of the phases can be retained up to a critical heating rate of 180°C/hr for our starting material and calcination set up. At heating rates above this critical rate, the homogeneity of the precursor is lost, expressing itself also in the low, $j_c$, of the processed material. The formation of the very inhomogeneous microstructures shown in
FIGURE 5c and f, is the consequence of melt formation during heating up to 850°C. Further evidences for melt are the large agglomerates of unreacted phases and the large ribbons of 22x1 with intercalated Bi-2212, as shown in FIGURE 5c and f.

During calcination, high heating rates and low pO₂ lead to the formation of a melt and substantially enhance 22x1 and Bi-2212 phase formation. At the same time this melt reduces the homogeneity of the precursor by enabling the formation of large grains and agglomerates. Inhomogeneous precursors yield low critical current densities, _j_c_. Thus to produce homogeneous precursors, melt formation during calcination has to be avoided.

The occurrence of melt during calcination leads not only to exaggerated grain growths of Bi-2212, 22x1 and other phases, but also to the inhomogeneous distribution of the chemical elements and the phases on large length scales in the precursor compacts. In order to quantify the homogeneity of the microstructures we used EDX analysis with different sizes of scanning areas. For each microstructure 3 different locations were analysed. The off-stoichiometry of the scanned area from the initial composition was calculated by adding up the differences of the stoichiometries analysed by EDX from the initial contents (Bi:2, Sr:2, Ca:1, Cu:2). In FIGURE 6 the off-stoichiometries are presented in dependence of the scanning areas. The off-stoichiometry for large scanning areas (10'000 μm²) from the ideal Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry is small and can be attributed to the uncertainty of EDX in multi-phase microstructures. A general increase in off-stoichiometry from the ideal Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry with decreasing scanning area characterizes the inhomogeneity of the precursor on different length scales. Up to a certain scanning area the off-stoichiometry only slightly increases. The critical scanning area (a_{crit}) indicates the length scale up to which inhomogeneities were present in the material or below which the material loses its homogeneity. The critical scanning area (a_{crit}) depends on the heating rate during calcination.

The critical scanning area (a_{crit}) of starting material that was heated with 900°C/hr is in the range of 2500 μm², whereas starting materials that were heated at lower rates (20, 180°C/hr) only start to lose their homogeneity in the range of 400 μm². For the smallest scanning area (1 μm²) the starting material heated with 180°C/hr is the least homogeneous compared to the others. These differences in homogeneity on this scale can be explained by the longer calcination time for the material heated at 20°C/hr enabling more phase formation and thus a more homogeneous distribution of the elements on the one hand and by the presence of melt strongly promoting phase
formation for the material heated at 900°C/hr on the other. However this melt is also responsible for the loss of homogeneity on a large scale. The strong loss of homogeneity in the unreacted material below the critical scanning area ($a_{\text{crit}}$) of 400 $\mu$m$^2$ is due to the particle size of around 5 $\mu$m.

Figure 6: Quantification of the homogeneity by EDX measurements of different scanning area of starting material heated with different heating rates to 850°C. Below a critical scanning area the off-stoichiometry strongly increases, corresponding to inhomogeneity in the precursor on this scale.

The results show that melt has to be avoided during calcination to retain the homogeneity of the starting mixture to the calcined precursor.

Instead of reducing the $pO_2$ during calcination by initiating rapid carbonate decomposition by high heating rates, a low $pO_2$ in the particle network can also be achieved by limiting the gas exchange with the furnace as in previous experiments. Starting material can either be calcined as loose powder or as a pressed pellet. Considering phase purity and short calcination times, pressed pellets will react faster than loose powders. On the other hand, the gas exchange will be reduced and the material will be less homogeneous. Therefore, all further precursors were calcined as loose powder in silver trays with a low packing density of around 1 g/cm$^3$. 

67
3.3.4. Influence of oxygen partial pressure during calcination on the critical current density of fully processed material

In order to investigate the influence of $p_{O_2}$ during calcination on the precursor homogeneity and on the critical current density $J_c$ of partial melt processed Bi-2212 material, starting material was heated to 710°C with a heating rate of 60°C/hr and annealed for 12 hrs in different $p_{O_2}$ ($10^{-2}$, 0.2 and 1 bar).

After the calcination all precursors were fine grained. Their colour varied from light grey for the precursor calcined in $p_{O_2}=1$ bar to black under reduced oxygen partial pressures. In FIGURE 7 the $J_c$ of fully processed material is shown in dependence of the oxygen partial pressure during the calcination of the precursor at 710°C for 12 hrs. Highest $J_c$ was achieved with the precursor annealed in air.

![Figure 7: Influence of the oxygen partial pressure during the calcination on the critical current density. Samples were annealed at 710°C for 12 hrs.](image)

The type of phases in all precursors were the same, 2201, 16580 and some unreacted SrCO$_3$ and CuO, however their amounts varied strongly and correlated to the colour of the precursor. With increasing oxygen partial pressure the amount of unreacted phases increases. Calcination at low and at high $p_{O_2}$ favours the 2201 phase formation whereas calcination at $p_{O_2}=0.2$ bar (air) favours the 16580 phase formation. Precursors with a high 16580 phase contents yield higher $J_c$ than those with...
high 2201 contents. We relate this behaviour to the platelet morphology of 2201 and that it is Ca free. Latter can be regarded as a reduction in the homogeneity of the element distribution in the precursor.

### 3.3.5. Influence of calcination temperature on $j_c$ of partial melt processed Bi-2212

The maximum calcination temperature of the loosely packed starting material has a prominent influence on the critical current density $j_c$ of fully processed material. In Figure 8 the critical current density is plotted in dependence of the calcination temperature. All precursors calcined between $710^\circ$C and $840^\circ$C yielded higher $j_c$ after partial melt processing than the reference material. $j_c$ increases with decreasing calcination temperature. An average $j_c$ of 7358 A/cm² was achieved with the precursor calcined at $710^\circ$C. Lower calcination temperatures led to very inconsistent results with low and high $j_c$.

![Figure 8: Influence of the calcination temperature on the critical current density. The error bars show maximum and minimum values of the 5 samples made of each precursor.](image)

X-ray diffraction was used to determine the phase composition of the calcination product. The phase composition strongly changes with increasing temperature. At $710^\circ$C the main phase is $\text{Bi}_{16}\text{Sr}_{5.44}\text{Ca}_{8.56}\text{O}_{38} (16580)$/$\text{Bi}_{14}\text{Sr}_{7}\text{Ca}_{5}\text{O}_{33} (14750)$ and 2201 besides unreacted SrCO$_3$ and CuO. The amount of unreacted SrCO$_3$ is below 10% as was calculated from the weight loss during the 12 hr annealing. Higher calcination temperatures lead to the dissolution of the 16580 and 2201...
becomes the main phase. Around 800°C, 91150 and Bi-2212 start to form and CuO disappears. At 840°C, Bi-2212 is the main phase besides some small amounts of 91150 and 2201. Line broadening of the Bi-2212 reflections indicates large amount of 2201 intergrowths in the Bi-2212, equal to non uniform stoichiometry and probably responsible for the wide peritectic decomposition temperature range found in many Bi-2212 precursors.

The linear decay of $J_c$ with increasing calcination temperature of the precursors can be accredited to the change in phase composition and particle growth as shown in FIGURE 9. At low calcination temperatures the particles are globular and the phases are distributed homogeneously on a length scale of 10 µm. With increasing calcination temperature the particles change their morphology from globular to platelet and the length scale on which the phases are separated increases. The change in particle morphology goes in parallel with the change of phase composition from the globular unreacted phases and 16580 to the platelet 2201 and Bi-2212. Latter is present in large ribbons built up of high aspect ratio at calcination temperatures of 840°C. Increasing amounts of large platelets of the layered compounds, 2201 and Bi-2212 have a negative influence on the properties of the precursor. With increasing calcination temperature the homogeneity of the precursor is reduced regarding particle morphology and length scale of phase separation.
Figure 9: Microstructures of starting material calcined at different temperatures. With increasing calcination temperature the grain size of different phases increases and so does the inhomogeneity of the samples.

The precursors were annealed for 12 hrs at the calcination temperature. For longer annealing times \( J_c \) does not further decrease as the results for precursors annealed at 840°C for different times showed. \( J_c \) for 12 hrs annealing show no significant difference to precursors annealed up to 48 hrs. This was also observed for precursors annealed at 710°C up to 36 hrs, although the phase composition changed strongly in contrast to the precursors annealed at 840°C.
3.4. Discussion

Precursors that yield fully processed Bi-2212 components with high critical current densities can be produced from binary oxide and carbonate starting material by avoiding melt formation during heating up to the calcination temperature and avoiding high calcination temperatures. DSC/TG measurements and thermodynamic calculations show that Bi$_2$O$_3$-CaO-CuO form an eutectic melt around 740°C at a pO$_2$ of 10$^{-2}$ bar. Such low pO$_2$ conditions are formed inside the particle network during the carbonate decomposition if the gas exchange with the air atmosphere of the furnace is insufficient. This is the case when the starting material is calcined with high green density or the crucible hinders gas exchange and provided the carbonate decomposition occurs in a short time interval due to too high heating rates. As CaCO$_3$ is the first compound that decomposes, it reduces the pO$_2$ and then the eutectic with Bi$_2$O$_3$ and CuO is formed.

Melt formation can be avoided by low green densities and moderate heating rates. High calcination temperatures also lead to the reduction of homogeneity. For the partial melt process and for the final homogeneity of the Bi-2212 compound the precursor must show maximum homogeneity just before it decomposes to the partial melt state during processing. This means, that one has to consider the heating up to the partial melt state as a further calcination step. During this heat treatment all precursors of nominal Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry react to the Bi-2212 phase independent of the initial phase composition [19]. At what temperature and at what rate the precursors react to Bi-2212 is determined by their phase compositions. Precursors with phase compositions other than 2201 and Bi-2212, as for instance achieved at low calcination temperatures, will react slower to Bi-2212. These Bi-2212 grains then do not have time to grow to platelets with high aspect ratio. However the precursors have to be nearly carbonate free as the precursors are compacted to green bodies of high density before they are partial melt processed to Bi-2212 components. Entrapped CO$_2$ will otherwise lead to melt formation at low temperatures with the same consequences as described for the calcination product.

Particles with high aspect ratio in the precursor amplify the inhomogeneity in the sample when it melts incongruently. The peritectic decomposition is a process that has to be nucleated. Nuclei for the decomposition are second phases, Bi-2212-2201 mixed state and grain boundaries. In a fully reacted precursor consisting of large particles the nuclei density is low and the nuclei are inhomogeneously allocated between the particles. During the consequently inhomogeneous decomposition the large particles of high aspect ratio, stacked to ribbons as shown in FIGURE 9d,
will attract and concentrate up the melt formed in their environment by capillary forces. This leads to agglomerates of the peritectic second phases $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{10}$ in the area from which melt was retracted and a phase separation on a 50 to 100 μm length scale. These inhomogeneities cannot be restored during partial melt processing despite the high volume fractions of 40 vol% melt. Upon cooling these inhomogeneities are even enhanced. Especially the slowly resolvable $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ phase found as clusters in the microstructures of fully processed material substantially reduces the current carrying cross-section and thus $j_c$.

Tailoring of precursor properties should be done under the guideline of obtaining the maximum homogeneity in the precursor just before the peritectic decomposition of 892°C. Calcination conditions yielding precursors from which components with high $j_c$ could be processed consisted of unreacted binary oxides and carbonates mixed homogeneously, calcined as loosely packed powder in a furnace where gas exchange is possible. Heating rates have to be adapted to the batch size, crucible geometry and furnace in order to obtain a calcination product free of carbonates. For initial material of Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry this can be achieved at calcination temperatures around 710°C in air, where first Bi rich phases like the $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ or $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{10}$ are formed. Higher temperatures, lower or higher $pO_2$ lead to the formation of 2201 and Bi-2212 which are less favourable calcination products due to their platelet grain morphology leading to phase separation.
3.5. Conclusions

In the first part of this paper the conditions for melt formation during calcination were outlined. The consequences of melt formation on the homogeneity of the precursor and finally on the critical current density $j_c$ of the partial melt processed compounds were studied in the second part. The results showed that homogeneous precursor powders will yield compounds with high $j_c$.

Homogeneous precursors can be obtained when melt is avoided during heating up of the starting material to the calcination temperature and at low calcination temperatures. Melt formation during the calcination strongly reduces the homogeneity in a short time and on a large length scale. This melt leads to the formation of second phase agglomerates and to large particles of high aspect ratio. A homogeneous high temperature state is the prerequisite for a homogeneous crystallization of Bi-2212 during cooling down and the formation of a percolating network of Bi-2212 platelets. The phase composition of a precursor determines whether homogeneity can be preserved during this heat treatment. The results show that phase compositions achieved at low calcination temperatures in air yield fully processed components of high $j_c$.

The results also showed that anything that leads to a reduction of the homogeneity of the precursor has a negative influence on $j_c$ of the melt processed material. The microstructures of Bi-2212 components that yield high $j_c$ are very homogeneous, have fine grains and low amount of residual second phases. The role of the precursor on the homogeneity of the melt processed Bi-2212 material is to enable a uniform peritectic decomposition to the partial melt state, in which the grain size of the high temperature phases 014x24 and 91150 is small and their distribution narrow and un-agglomerated.

In future work the influence of precursor phase composition will be studied in more detail. The results of this work indicate that by adjusting the phase composition of the precursor we have a powerful tool to take influence on the precursor reactions that take place when partial melt processing the material.
Chapter 3: Influence of Precursor Calcination Parameters on the Critical Current Density of Bi-2212 Superconductors

References


Chapter 4

Novel Precursor Reaction Pathways to Bi-2212 Bulk Superconductors

Abstract

Precursors of defined phases composition were produced by separate calcination of compounds that complete each other to the Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry. The critical current densities ($J_c$) of thick film material processed from these precursors range from 6000 to 8000 A/cm$^2$ (10 μV/cm). It was found that precursors with phase compositions that form rapidly Bi-2212 platelet grains yield lower $J_c$ than phase compositions that react sluggishly. The different reactivities can be associated to different reaction pathways to the Bi-2212 phase. Rapid Bi-2212 phase formation is a consequence of melt assistance, which favours a high aspect ratio of the grains. The different $J_c$ achieved by the precursors can therefore be attributed to the different particle aspect ratios and the different nuclei densities for the peritectic decomposition that have an influence on the homogeneity of the partial melt state.
4.1. Introduction

Recent work [1], [2] indicates that only homogeneous Bi-2212 precursors can yield partial melt processed components with high critical current densities ($J_c$). In calcination experiments with unreacted mixtures of oxides and carbonates it was shown that partially reacted precursors yield Bi-2212 components with higher $J_c$ than fully reacted precursors consisting of Bi-2212 particles of high aspect ratio. The partially reacted precursors are nearly carbonate free and consist of homogeneously mixed small particles of different phases. The green bodies made thereof react to Bi-2212 during the heating to the high temperature state. From these results we draw the conclusion that shortly before it peritectically decomposes at 892°C the precursors should be homogeneous on a small length scale.

These experiments further showed that the homogeneity of a precursor is reduced by high aspect ratio Bi-2212 platelets stacked to large ribbons that form at high calcination temperatures (840°C). Highest $J_c$ were achieved with precursors that were calcined at 710°C in air and consist mainly of $\text{Bi}_{10}\text{Sr}_{5.44}\text{Ca}_{8.56}\text{O}_{38}$ (16580)/ $\text{Bi}_{14}\text{Sr}_{7}\text{Ca}_{4}\text{O}_{33}$ (14750) and 2201 besides small amounts of unreacted SrCO$_3$ and CuO. The heating during partial melt processing has to be considered as an additional calcination step during which precursors that react sluggishly to Bi-2212 will remain homogeneous.

The adjustment of the precursor phase composition gives us a powerful tool to control the rate of Bi-2212 formation during this additional and final calcination step. However the use of oxide and carbonate mixtures of Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry only allows us to study of a limited number of phases (16580, 2201, 014x24 and Bi-2212). Therefore in this work a two component approach was chosen. This was done by the separate preparation of phases pairs from the Bi-Sr-Ca-Cu-O system that are mixed together and complete each other to the Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry. Such a two step precursor production route has already been applied by various authors [3], [4], [5], [6] for Bi-2212 and is very common for Bi,Pb-2223 [7], [8], [9], [10].

However in contrast to the precursors of nominal Bi,Pb-2:2:2:3 stoichiometry, where only minor amounts of melt are formed during the high temperature treatment, the precursors of Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry react already at lower temperatures to Bi-2212 before then decomposing to the peritectic phases, 014x24 + 91150 and a melt. In the partial melt state the material is close to the thermodynamic equilibrium due to the high content of melt (35 vol.%) [11], [12]. Therefore one can expect that the precursor has only has an influence on the homogeneity of
Chapter 4: Novel Precursor Reaction Pathways to Bi-2212 Bulk Superconductors

the partial molten state and not on its phase composition. The precursor should then only influence the uniformity and temperature range of the transition to the partial melt state [1] which designates the particle size and spatial distribution of the peritectic phases. However it was found that in case large \( \text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2 \) phase particles are present in the precursor, these grow in the partial melt state and then only partially dissolve during Bi-2212 crystallization upon cooling [13], and homogeneity is lost in the final product resulting in low \( j_c \).

The objective of the present work is to determine precursor phase compositions that react sluggishly to Bi-2212 of platelet form and therefore can preserve the initial homogeneity of the precursor to the high temperature state. The nominal stoichiometry of the studied precursors are always Bi:2, Sr:2, Ca:1, Cu:2 but their phase compositions differ strongly.

Melt formation during calcination leads to a rapid loss of homogeneity and Bi-2212 formation. To avoid low eutectic liquids, that favourably form between Bi-, Ca- and Cu oxides, during the calcination of the precursors, mainly phases consisting of Bi-, Sr- and Ca oxides on the one hand and on the other hand Sr-, Ca- and Cu oxides were produced.

The results show, that those precursors consisting of Bi-poor and on the other hand of Cu-rich compounds react sluggishly to Bi-2212 upon heating and yield Bi-2212 components with high \( j_c \). It was found that the reaction rate to Bi-2212 during heating to the high temperature state is strongly determined by the presence of melt.
4.2. Experimental

The precursors from which samples are processed were all of Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry. They were made up of two separately produced precursors each of which one is single phase and the other is completing the composition to Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry. The single phase precursor was calcined until only the desired phase was found by XRD. The complementing precursor was calcined until no more unreacted oxides and carbonates were found by XRD. The calcination of both precursors was done keeping the temperatures as low and the times as short as possible to avoid melt formation, particle coarsening and Bi evaporation. The stoichiometries of the precursors are listed in TABLE 1. SP is short for Single Phase and Co for Completing batch. The hyphenated phases in the name were the aimed phase. The Bi-and Cu-contents in fraction of atoms and the Sr/Ca ratio of the precursors are additionally listed to simplify the orientation in the isothermal cross-section (FIGURE 3). The Bi and Cu contents were calculated by dividing the number of Bi or Cu atoms with the sum of all elements of the stoichiometric unit. As a reference precursor, fully reacted Bi-2212, noted as “SP 2212” of Solvay was used.
## Table 1: Stoichiometric composition and Bi-, Cu- content and the Sr/Ca ratio of the precursors. SP is short for Singe Phase and Co for Completing. The hyphenated phases of the name were the aimed phase. The Bi and Cu contents were calculated by dividing the number of Bi or Cu atoms with the sum of all elements of the stoichiometric unit.

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<th>Ca</th>
<th>Cu</th>
<th>Bi content</th>
<th>Cu content</th>
<th>Sr/Ca ratio</th>
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<td>3.81</td>
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<td>0.29</td>
<td>2</td>
</tr>
</tbody>
</table>

Chapter 4: Novel Precursor Reaction Pathways to Bi-2212 Bulk Superconductors
As starting powders Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$ and CuO attained from Solvay were used. They have a purity >99.98% and a typical particle size range of 1 - 7 µm. The starting oxides and carbonates were mixed to the desired stoichiometry and gently ball milled in plastic jars with ZrO$_2$ balls. As a solvent butylacetate (Fluka, purum) was used with 1-2 wt% Span 80 (Fluka) as a dispersion agent. After milling the slurries, the solvent was slowly evaporated during milling to avoid sedimentation by gently blowing air into the open milling jars. The dispersion agent was slowly burnt out in a large glass bowls at 350°C for 24 hrs.

The unreacted mixtures were calcined in silver trays in loosely spread batches of 15 - 20 g. The packing height varied between 10 - 20 mm with a density of 1 g/cm$^3$. After calcination the precursors were milled in an agate mortar and pestle by hand and sieved (63µm). No ZrO$_2$ particles were found in the precursors and no Zr was detected by EDX measurement.

The calcination parameters were determined separately for each precursor by DSC measurement in air. The calcination temperature was chosen 20°C below the first (melting) peak of the oxide and carbonate mixture. The heating rate to the desired temperature was 60°/hr and the calcination time was 12 hrs per calcination step, the calcination atmosphere was air. If the mixture reacted to the desired phase (SP) or all carbonates had decomposed (Co), the calcination was terminated.

After the calcination the single phase and completing precursor were mixed together in right amounts to achieve the Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry. From these precursors 5 samples were made by uniaxially pressing (250 MPa) the precursor into pellets. The samples were partial melt processed on Ag substrate to the sequence shown in FIGURE 1. The sample dimensions were 13 mm in diameter with an initial thickness of 700 µm and a final thickness of around 400-500 µm after processing.
Figure 1: Temperature, time and atmosphere program of the partial melt process used in this study.

Critical current density $j_c$ of the processed samples was measured with an AC-magnetometer, using the 10 $\mu$V/cm criteria ($j_c$ is about 30% higher than measured with the 1 $\mu$V/cm criteria). The microstructures were analysed by SEM (Leo 1530) on polished samples and the volume content of second phases determined by the mean intercept method (Lince Software).

The calculation of the isothermal cross-section at 880°C was done with ThermoCalc using the database assessed by the CALPHAD approach [11].

To study the reactivity of the precursors during heating to the partial melt state, the samples were quenched at 800, 850 and 880°C. The samples were processed in air and air quenched to room temperature by removing them from the furnace. These samples were analysed by XRD at the SLS in Grenoble using a wave length of 0.72 Å and by DSC/TG (Netzsch STA449C Jupiter) measurements performed in oxygen with a heating rate of 10°/min.
4.3. Results and discussion

4.3.1. Precursor properties

The phase compositions of the single phase and completing precursors are listed in Table 2. It was not possible to produce the aimed phase for all "single phase" (SP) precursors and therefore some of them were multi-phase too, but all the completing precursors were carbonate free. The microstructures of two precursors after mixing and pressing the SP and Co precursors are shown in Figure 2. They show particles of 3 - 7 μm that are homogeneously mixed on a 10 μm scale. EDX analysis of large areas (500x500 μm) showed deviations from the Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry to be below ±3 at%.

![Figure 2: Microstructure of unprocessed and pressed mixtures of single phase (SP) and completing (Co) precursor (backscatter SEM image).](image)

During heating to the partial melt state these phases will react to Bi-2212 following different reaction pathways before then peritectically decomposing to 014x24, 91150 and melt.

4.3.2. Influence of the precursor phase composition on the critical current density of fully processed Bi-2212

The critical current densities \( J_c \) of fully processed Bi-2212 material from the different precursors are presented in Table 2. The results show that \( J_c \) strongly depends on the phase composition of the precursor. With the phase combination 22x1, x=0.4 and 01x1, x=0.6 (SP 22x1+Co) superconducting Bi-2212 material with \( J_c \) over 8000 A/cm\(^2\) was produced, whereas with the phase combination of 01x1, x=0.35 and 2100, 6200 (SP 01x1+Co) only \( J_c \) around 6000 A/cm\(^2\) was achieved. However, reactive precursors were all better than material that was processed from a fully reacted Bi-2212 precursor which yielded a \( J_c \) of around 5000 A/cm\(^2\).
<table>
<thead>
<tr>
<th>Code</th>
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<th>Std. dev.</th>
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<td>SP &quot;91150&quot;</td>
<td>14750, SrCO$_3$</td>
<td></td>
<td>7234</td>
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<td></td>
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<tr>
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<tr>
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<td>2001, Bi$_2$O$_3$</td>
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<tr>
<td>SP &quot;2212&quot;</td>
<td>Bi-2212</td>
<td></td>
<td>5287</td>
<td>329</td>
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</table>

**Table 2:** Phase composition of the precursors and $J_c$ of fully processed samples thereof.
In order to correlate the $j_c$ to the different reaction pathways an isothermal cross-section of the BiO$_{1.5}$-Sr$_{2/3}$Ca$_{1/3}$O-CuO system at 880°C in oxygen is shown in FIGURE 3. The star represents the Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry and phase. The dotted area is the stability range of melt in coexistence with solid phases and the crossed area is the stability range of melt only. The symbol free phase fields do not contain any liquid in equilibrium. On the axis BiO$_{1.5}$-Sr$_{2/3}$Ca$_{1/3}$O the obtained $j_c$ is plotted against the Bi content of the Cu-free or Bi-rich phases (TABLE I). Accordingly $j_c$ is plotted against the Cu content of the Bi-free or Cu-rich phases on the axis CuO-Sr$_{2/3}$Ca$_{1/3}$O (TABLE I). An example how to read this plot is shown with the precursor “SP 8110 + Co” where the single phase compound 8110 is mapped in dependence of its Bi content (left plot) and the completing phases (01x1 and 02x1) designated as Co “8110” in dependence of the average of their Cu content. The connection of the SP and Co precursors in the cross-section is a line that passes through the composition of Bi-2212 (star). The two precursors will react to Bi-2212 as they make up together the Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry using their appropriate amounts.

**Figure 3:** Isothermal cross-section of the BiO$_{1.5}$-Sr$_{2/3}$Ca$_{1/3}$O-CuO at 880°C in oxygen with the critical current densities $j_c$ in dependence of the Bi and Cu contents of the single phase (SP) and completing (Co) precursors. The “star” represents the Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry, the “dotted area” is the stability range of melt with solid phases, the “crossed area” is the stability range of melt. (Calculated phase diagram using the CALPHAD approach [11])
Precursors from which high \( j_c \) material was processed consisted of single phase and completing precursors that were Bi-poor or Cu-rich. Best \( j_c \) were achieved with compounds that had Bi contents between 0.5 and 0.4 and Cu contents between 0.5 and 0.7 (FIGURE 3).

As this isothermal cross-section has a Sr to Ca ratio of 2, however many of the phases have different ratios (TABLE 1) they actually cannot be shown here and were just transposed into this cross-section. The results show that \( j_c \) is also sensitive to the Ca and Sr content of the phases. This can be seen in the precursors “SP 16580+Co” and “SP 2110+Co” were the phase compositions are nearly the same, however \( j_c \) differ strongly. Similar behaviour is found for the precursors “SP IL+Co” and “SP 22x1+Co” where the 22x1 phase only differs in Ca content.

The results also support the finding of the calcination experiments [2]. Mixtures of oxides and carbonates in Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry were calcined at different temperatures. The \( j_c \) of processed Bi-2212 material of the precursor annealed at 710°C was the highest with 7358 A/cm\(^2\) compared to other annealing temperatures. The phase composition of this precursor was rich in 16580 and 14750 phase. The \( j_c \) obtained is similar to \( j_c \) of material processed from precursors with the composition made up by the 16580 and 14750 phases (“SP 2110+Co”, “SP 91150+Co” and partially “SP 16580+Co”, TABLE 2).

The different \( j_c \) can be explained regarding the reactivity of the different phase compositions during heating to the partial melt state. Therefore the samples were quenched during heating and their phase compositions and microstructures studied.

4.3.3. Bi-2212 phase formation during heating to the partial melt state

During heating to the partial melt state the phases in the precursors react to Bi-2212. Quenching experiments have shown that at temperatures close to the peritectic decomposition temperature (892°C in oxygen) all the precursors have reacted to Bi-2212. The reaction pathway of the precursors to Bi-2212 starts with the formation of the 22x1 phase at temperatures below 800°C which then starts to transform to Bi-2212 between 800 and 880°C. Upon further increasing the temperature, the Bi-2212 then peritectically decomposes to 014x24, 91150 and a melt at 892°C. The reactivity of the precursors depends on their phase compositions, shown in FIGURE 4, representative for the reaction pathway of the precursors “SP 01x1+Co”, “SP 014x24+Co”, “SP 8110+Co” and “SP 016580+Co”. The precursors were chosen for the different Bi and Cu contents of the single phase compound and the resulting different \( j_c \). In the FIGURE 4a, c, e the reflections of
2201 and of Bi-2212 and in the FIGURE 4b, d, f the reflections of 01x1 and of 014x24 are shown from samples quenched at 800, 850 and 880°C. The single phase compounds of “SP 01x1+Co”, “SP 014x24+Co” differ mainly in the Cu content, 0.5 for 01x1 respectively 0.63 for 014x24. Their unlike reactivity can be seen in FIGURE 4b and d. At 800°C the precursors have started to react as indicated by the 22x1 and 2201 peaks but the samples still contained unreacted phases as indicated by the large 01x1 and 014x24 peaks. At 850°C the 01x1 peaks have merely disappeared in contrast to the present 014x24 peaks. Comparing the amount of Bi-2212 and 22x1 already formed at 850°C by the peak intensities, the “SP 01x1+Co” precursor has much more Bi-2212 and 22x1 than the one made from “SP 014x24+Co”. Therefore the latter precursor, consisting of a Cu-rich compound, reacts much more sluggishly to Bi-2212. Very similar observations can be made for the precursors “SP 8110+Co” and “SP 16580+Co” where the single phase precursors mainly differ in Bi content, 8110 phase with 0.8 Bi content and 16580 with 0.53. Here the precursor with the Bi-rich compound 8110 reacts faster to 22x1 and then to Bi-2212 as can be seen in FIGURE 4a, b and c compared to the precursor with the Bi-poorer compound 16580. At 800°C no Bi-2212 has formed in the latter precursor in contrast to the other precursors. At 880°C the main phase for all precursors is Bi-2212 but the amounts of unreacted phases differ. The slightly shifted peak positions of the 22x1 and Bi-2212 phase during the initial formation is a consequence of different Bi-2212 stoichiometries. This indicates that the Bi-2212 single phase region is being entered from two different sides in the compositional space.
Chapter 4: Novel Precursor Reaction Pathways to Bi-2212 Bulk Superconductors

Figure 4: Reaction pathway of the “SP 01x1+Co”, “SP 014x24+Co”, “SP 8110+Co” and “SP 016580+Co” precursors to Bi-2212 during heating to the partial melt state (895°C) in air. The precursors were quenched at 800, 850 and 880°C.

Correlating the results with $J_c$ of processed material shows that precursors that react sluggishly, and therefore at higher temperatures to Bi-2212, yield higher $J_c$. The precursors “SP 016580+Co”, “SP 014x24+Co” react slowly and achieve $J_c$ of 6444 and 6791 A/cm$^2$. The precursors “SP 01x1+Co” and “SP 8110+Co” have Cu-poor and Bi-rich compounds and react rapidly to Bi-2212 and achieve $J_c$ of only 5914 and 6031 A/cm$^2$.

The reason for the rapid reaction of precursors with Bi-rich and Cu-poor phases can be found in the isothermal cross-section shown in FIGURE 3. The reaction pathway of these phases pass through phase fields in which melt co-exist, close to the single phase region of melt that spreads out from the BiO$_{1.5}$ corner with increasing temperature. Consequently the reactions of these precursors
is promoted by transient melts. On the other hand, the reaction pathways of precursors with Cu-rich and Bi-poor phases are further away with their reaction pathway from the melt regions as shown by the example in FIGURE 3 and therefore react sluggish to Bi-2212.

In order to investigate the influence of the precursors on the reaction rate and pathways, DSC experiments were performed.

4.3.4. Peritectic decomposition of the reacted precursors

A homogeneous high temperature state in which the peritectic phases are fine grained and evenly distributed is the prerequisite for the formation of a high current carrying cross-section in fully processed Bi-2212. The partial melt state is a consequence of the peritectic decomposition of the precursor. Therefore it can be expected that the homogeneity of a precursor before it peritectically decomposes at 892°C defines the homogeneity of the high temperature molten state. The transition to the partial melt state can be monitored by DSC measurements. Precursors were heated in air to 880°C following the partial melt process and quenched in air to room temperature. The DSC experiments were performed in O₂ with a heating rate of 10°C/min. In contrast to the fully processed samples that were processed on Ag, the experiments were performed using Al₂O₃ crucibles as no Ag crucibles are available for the temperature range of 900°C. This surely has an effect on the peritectic decomposition temperature of the precursor as the contact with Ag lowers the decomposition temperature by 25°C [14], but can be neglected for the moment.

In FIGURE 5 the DSC results of the “SP 22x1+Co”, “SP 014x24+Co” and the fully reacted Bi-2212 precursor “SP 2212” are shown. General trends can be formulated from these data that were confirmed with other precursors. The peritectic decomposition peak can be separated into two overlapping events. For the “SP 22x1+Co” precursor these events can clearly be distinguished and for the “SP 2212” precursor they can hardly be perceived. The event occurring at lower temperatures corresponds to the melting of 2201 either as a separate phase or integrated in the mixed state with Bi-2212. The purer the Bi-2212 phase is before the decomposition, the less pronounced this decomposition of the mixed state is and the higher the amount of energy that has to be brought up to decompose the precursor and its transition to the partial melt state. The fully reacted precursor “SP 2212” decomposes in a relative narrow temperature range and the energy required for the transition is 92 J/g, the highest compared to the decomposition of “SP 014x24+Co” or “SP 22x1+Co”.
Latter precursors already have a higher enthalpy due to phase formation during heating and decompose in a broader temperature range. The energy needed for the decomposition are consequently lower, 87 J/g for “SP 014x24+Co” and 82 J/g for “SP 22x1+Co”.

The results clearly show that precursors decompose in different manners to the partial melt state. The phase composition of “SP 22x1+Co” and “SP 014x24+Co” precursor after quenching from 880°C is mainly Bi-2212 with still some unreacted 22x1 and 01x1 respectively 014x24. These compounds that react sluggishly and only at high temperatures to Bi-2212 form fine grained and highly defective Bi-2212. This defective Bi-2212 needs less energy to decompose to the high temperature state than perfect Bi-2212. Remarkable is that those defect rich Bi-2212 powder grains result in components which yield higher \(J_c\) (8461 A/cm² for “SP 22x1+Co” and 6791 A/cm² for “SP 014x24+Co”) than precursors that transform in a narrow temperature range and with high energies (5287 A/cm² for “SP 2212”).

The peritectic decomposition is a process that needs to be nucleated. Peritectic second phases in the precursor and material imperfections such as the mixed state of Bi-2212 are such nuclei. Fully reacted precursors with perfect Bi-2212 grains and only some second phases have a low nuclei density. Consequently the melting of such a precursor is inhomogeneous resulting in an
inhomogeneous partial melt state. Whereas imperfect Bi-2212 and many small grains of secondary phases are ideal nucleation sites for melt formation. Precursors with high nuclei density decompose over a broader temperature range and more uniformly resulting in a homogeneous partial melt state. This leads to homogeneously processed microstructures and higher $J_c$.

4.3.5. Influence of precursor phase composition on the microstructures of fully processed Bi-2212

The consequence of a homogeneous or inhomogeneous high temperature state can be seen in the homogeneity of the fully processed material, especially regarding $\text{01424}$ second phase volume content, distribution and grain size. Therefore the microstructures of fully processed material originating from the rapidly reacting precursor “SP 01x1+Co” and the sluggishly reacting precursor “SP 014x24+Co” were compared. In the microstructures of fully processed material there are always residual second phases. The residual second phases are the consequence of an incomplete Bi-2212 crystallization during cooling down from the partial melt state. The inhomogeneous distribution of the peritectic second phases, as well as their broad particle size distribution in the high temperature state is one of the main reasons of this incomplete crystallization.

In FIGURE 6 the microstructures of fully processed Bi-2212 from the precursors “SP 01x1+Co” and “SP 014x24+Co” are presented. FIGURE 6a is an overview picture showing the $\text{01424}$ second phase present in 2 different spacial arrangements, once in large clusters of 50 to 300 $\mu$m in size and finely dispersed as single grains with an average grain size of 5 $\mu$m. The $\text{01424}$ clusters are agglomerates of $\text{01424}$ grains, that were either formed during the peritectic decomposition as described above or during the Bi-2212 crystallization. In the latter case the $\text{01424}$ grains are pushed together by the rapidly growing Bi-2212. In TABLE 3 the results of the quantification of microstructures are listed regarding volume fraction and grain size of the single $\text{01424}$ grains and of $\text{01424}$ clusters. Only the residual second phase $\text{01424}$ was considered in this study and not $\text{91150}$, as XRD measurements of the samples only show minor amounts of this phase and because its grains are hardly visible in the Bi-2212 matrix.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>$\text{01424}$ grains [vol.%]</th>
<th>Grain size [\mu m]</th>
<th>$\text{01424}$ clusters [vol.%]</th>
<th>$J_c$ [A/cm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>“SP 01x1+Co”</td>
<td>9</td>
<td>5</td>
<td>8</td>
<td>5914</td>
</tr>
<tr>
<td>“SP 014x24+Co”</td>
<td>5</td>
<td>5</td>
<td>2</td>
<td>6791</td>
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</table>

Table 3: Quantification of the fully processed Bi-2212 of the precursors “SP 01x1+Co” and “SP 014x24+Co”. 
Figure 6: SEM microstructures of fully processed Bi-2212 from the precursors “SP 01x1 + Co” and “SP 014x24+Co”. Image (a) shows the two kinds of 014x24 second phases, large clusters and single grains.

The material processed from the “SP 01x1+Co” precursor has a slightly higher amount of residual 014x24 grains and a substantially higher amount of clusters than material processed from the “SP 014x24+Co” precursor. Both the larger amount of single residual 014x24 grains and clusters are responsible for the lower \( J_c \) of the material processed from this precursor. However the large difference in the amount of clusters should show a much larger difference in \( J_c \). The residual second phases have a deteriorating effect on \( J_c \) by reducing the current carrying cross-section and the number of percolating Bi-2212 networks.

It is surprising that the precursor “SP 014x24+Co” consisting of the peritectic second phase 014x24 yields processed material with less residual 014x24 and therefore higher \( J_c \) than the 014x24 free precursor “SP 01x1+Co”.
4.4. Summary and Discussion

All precursors react to Bi-2212 during heating to the high temperature state (895°C), independent of their initial phase composition. The temperature and rate at which this reaction starts and proceeds strongly depends on the phases present in the precursor. Upon further heating the formed Bi-2212 then peritectically decomposes to the high temperature phases (014x24 and 91150) and a melt. For all the precursors, the phase compositions (014x24: 27 vol%, 91150: 36 vol% and melt: 37 vol%) in the high temperature state was the same. After a homogenization period of 2 hrs. in the partial melt state new Bi-2212 crystallizes during cooling down from 895 to 850°C. It can therefore also be expected that the precursor phase composition does not have an influence on the crystallization temperature of Bi-2212 upon cooling down from the partial melt state. Finally after the annealing steps the material yields, \( J_c \), that vary depending on the phase composition of the precursors. Reasons for an influence of the precursor phase composition on \( J_c \) of fully processed material is found in their reactivity to Bi-2212 and the different peritectic decomposition behaviour. Other reasons were excluded, like: (a) Off-stoichiometry and poisoning, since all precursors were produced the same way or (b) harmful second phases, because precisely from precursors with these phases (014x24, 91150 and 22x1) highest \( J_c \) have been achieved.

It can therefore be summarized that precursors with phase compositions that react at low temperatures and rapidly to 22x1 and then to Bi-2212 yield lower \( J_c \) than phase compositions that react sluggishly. The reactivity of a phase composition can be judged by the Bi and Cu content of its phases, determining the reaction pathway. If this reaction pathway cuts through or is close to a melt rich region in the phase diagram during heating, then the 22x1 and Bi-2212 formation is accelerated and additionally particles of high aspect ratio are promoted. Grain growth of 22x1 and Bi-2212 is very anisotrop for both phases, due to their layered crystal structure. In-plane (a, b) growth is much higher than in c direction. In FIGURE 7 the 22x1 and Bi-2212 formation, transformation and growth is illustrated in a solid state and in a melt assisted reaction. In the solid state reaction the growth in a, b direction is limited by the diffusion of the elements along the grain surfaces, whereas in the case of the melt assisted reaction, the elements can rapidly diffuse through the melt to the fast growing a, b planes and consequently forming grains with high aspect ratios.
Chapter 4: Novel Precursor Reaction Pathways to Bi-2212 Bulk Superconductors

Figure 7: Sketch of Bi-2212 formation and growth: (a) In the solid state and (b) in melt assisted environment.

We explain the negative influence of early Bi-2212 formation on $J_c$ in the increasing aspect ratio of the Bi-2212 particles at temperatures above 800°C and in the reduction of nuclei density. Both effects can be regarded as a loss of homogeneity in the precursor and thus in the green body and are responsible for the formation of an inhomogeneous partial melt state. Calcination experiments [2] have shown that Bi-2212 platelets grow to large ribbons of up to 50 µm length and the few second phases are distributed between the ribbons. This configuration of the phases will amplify the inhomogeneity induced by the peritectic decomposition as shown in FIGURE 8. The decomposition of the precursor to the peritectic solid phases and a melt is a nucleated process and therefore already inhomogeneously distributed in the green body. Nuclei for this decomposition are peritectic second phases and material imperfections such as 2201 and the mixed state. In precursors that have rapidly reacted to Bi-2212 and had time to form large and perfect ribbons of aligned Bi-2212 platelets it can be expected that the peritectic decomposition starts around the peritectic second phases (FIGURE 8a). The ribbons consisting of densely packed particles of platelet morphology and high aspect ratios then drain up this freshly formed melt by capillary forces and leave behind the peritectic second phases (FIGURE 8b). Consequently this will lead to an agglomeration of peritectic second phases (clusters in FIGURE 6a) and a demixing of the elements on a large scale which can only partially be restored in the partial melt state.
The crystallization of a high fraction of percolating networks of Bi-2212 grains is only possible from a homogeneous partial melt state. This is not possible from a partial melt state in which the second phases are partially agglomerated and the particle sizes vary strongly as these second phases will only partially dissolve and consequently reduce the current carrying cross-section. The high $j_c$ achieved for the “SP 22x1+Co” precursor supports this picture. The precursor consists of globular particles of 22x1 and the completing 01x1 phase, which react sluggishly upon heating to Bi-2212 by intercalating Ca and Cu. The particle morphology and size are retained as the reaction pathway is far from the single phase melt region. Therefore the green bodies of Bi-2212 originating from this precursor consist of particles of low aspect ratios with many material defects and finely distributed second phases prior the peritectic decomposition reaction at high temperatures. Therefore this precursor does not amplify inhomogeneity in the already inhomogeneous peritectic decomposition.
4.5. Conclusions

Precursors of different phase compositions with Bi-2212 stoichiometry have been produced. The precursors have been characterized regarding phase composition, homogeneity and reactivity to Bi-2212 upon heating. All precursors react to Bi-2212 before peritectically decomposing to the partial melt state. The partial melt processed samples thereof however show a wide range of critical current densities $J_c$ that can be correlated with the amount of residual second phase particles and clusters found in the microstructures.

It can be stated that precursors that react sluggishly to 22x1 and Bi-2212 yield fully processed material with higher $J_c$. Such precursors consist of Bi-poor and Cu-rich compounds that have reaction pathways to Bi-2212 that do not cross melt rich regions in the phase diagram. This yields precursor particles with low aspect ratio and a high density of nuclei for the peritectic decomposition. The homogeneity of the peritectic decomposition is determined by the precursor. Inhomogeneous decompositions result in a wide particle size distribution and clusters of the peritectic phases in the high temperature state. The clusters form as a consequence of capillary forces built up between densely packed Bi-2212 particles with high aspect ratios, draining locally formed melt and leaving behind agglomerates of second phase particles.

$J_c$ of over 8000 A/cm² have been achieved in bulk Bi-2212 with a precursor consisting of 22x1 and 01x1 compounds. This promising result confirms the importance of the precursor on the peritectic decomposition to the high temperature state and finally on the homogeneity and current carrying capability of the fully processed material.
Chapter 4: Novel Precursor Reaction Pathways to Bi-2212 Bulk Superconductors

References


Chapter 5

Enhanced Residual Second Phase Dissolution by Atmosphere Control in Bi-2212 Superconductors

Abstract

For power applications, where high current carrying capabilities are required and therefore thick film and bulk material are called for, the Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_{8+y}$ (Bi-2212) compound has evolved as one of the most promising. During partial melt processing the crystallization from the partial melt state upon cooling is incomplete, due to the stability of 014x24 and sterically hindered diffusion and redistribution of melt originating from the highly anisotropic crystallizing Bi-2212 platelets. Therefore, considerable amounts of residual 014x24 and “4413”, the mixed state of Bi-2212 and 2201, and residual melt are present in the microstructures at 850°C. The subsequent annealing in oxygen leads to a limited dissolution of 014x24 phase and the conversion of “4413” to Bi-2212. Thermodynamic calculations of BiO$_{3/2}$Sr$_{2/3}$Ca$_{1/3}$O-CuO cross-sections at 850°C at different pO$_2$ by the CALPHAD method show that the stability range of 014x24 depends highly on the oxygen partial pressure (pO$_2$). These results correlate perfectly with the experimental observations. By annealing at low pO$_2$ (0.1 bar) after crystallization, the amount of residual phases is reduced by more than 50% and the critical current density of the fully processed material increases by 65% compared to material annealed at high pO$_2$ (1 bar). This increase is attributed to a gain of current carrying cross-section as a consequence of enhanced 014x24 dissolution.
4.1. Introduction

Among the vast number of high temperature superconducting compounds the Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_8$ (Bi-2212), Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ (Bi-2223) and Y$_1$Ba$_2$Cu$_3$O$_6$ (Y-123) have emerged as the most promising compounds for industrial applications. For power application where primarily high current carrying capability are required, thick films and bulk material of Bi-2212 have evolved as the most promising for first applications [1].

The parameters of the partial melt process of Bi-2212 have been the subject of extensive study. Besides temperature and time, the atmosphere is crucial for obtaining high current carrying capacity. Especially the control of $pO_2$ during the final stage of processing, introducing oxygen vacancies necessary for superconductivity, has been subject of detailed studies [2].

The Bi-Sr-Ca-Cu-O system is home to a large number of phases. Their nature and stability have been excessively studied [3], [4], [5], [6], [7], [8], [14], [20]. The formation and distribution of the phases in the microstructure of the final Bi-2212 component can be controlled to a certain extent by the processing parameters. An example is the lowering of the melting temperature from 890°C to below 800°C by reduction of the oxygen partial pressure [9], [10], [11]. The most important phases present during partial melt processing of Bi-2212 are listed in TABLE 1.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
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<td>Bi-2212</td>
<td>Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_8$</td>
<td>High $T_c$ compound, 2 CuO layers</td>
</tr>
<tr>
<td>2201</td>
<td>Bi$_2$Sr$_2$Cu$_1$O$_6$</td>
<td>Low $T_c$ compound, 1 CuO layers</td>
</tr>
<tr>
<td>&quot;4413&quot;</td>
<td>Bi$<em>4$Sr$<em>4$Ca$</em>{1+X}$Cu$</em>{3+X}$O$_{14}$</td>
<td>Random mix of the 1 and 2 layered compound</td>
</tr>
<tr>
<td>22x1</td>
<td>Bi$_2$Sr$_1.6$Ca$_0.4$Cu$_1$O$_6$</td>
<td>Composition of the peritectic liquid (melt)</td>
</tr>
<tr>
<td>014x24</td>
<td>Sr$<em>{14.5}$Ca$<em>8$Cu$</em>{24}$O$</em>{38}$</td>
<td>Bi-free peritectic second phase</td>
</tr>
<tr>
<td>91150</td>
<td>Bi$<em>9$Sr$</em>{11}$Ca$<em>5$O$</em>{30}$</td>
<td>Cu-free peritectic second phase</td>
</tr>
</tbody>
</table>

Table 1: Abbreviation, composition and nature of phases important in this work.

In partial melt processing under pure oxygen the peritectic decomposition of Bi-2212 starts at 890°C. A Bi-free phase (014x24), a Cu-free phase (91150) and a liquid are present in the high temperature state (partial melt state). During slow cooling from 890°C to 850°C, 014x24 and 91150 have to dissolve while Bi-2212 crystallizes from the melt [12]. For several reasons this reaction is incomplete and residual second phases, among them 014x24 and 2201 are detected in the microstructure.
The 014x24 grains dissolve slow and incomplete, due to their size and stability. Even after annealing for long times at 850°C in oxygen a certain amount of 014x24 remains in the microstructure. [13].

2201 is found as separate grains but also embedded as intergrowths in Bi-2212. Heeb et al. report of Bi-2212 grains with low amount of 2201 intergrowths (5%) but also of grains consisting of 30 to 70% intergrowths [14], [15]. 2201 is formed as a consequence of the slow 014x24 dissolution and the sterically hindered diffusion of elements in the residual liquid, due to crystallized Bi-2212 sheets as described by Rikel et al. [16]. They propose that initially Bi-2212 is precipitated in the melt, depleting it from Cu and Ca, allowing only 2201 to form, as the lacking elements are bound in 014x24. The result is Bi-2212 with many 2201 intergrowths known as the mixed state or the “4413” phase.

In most of the processed thick film and bulk material, the current carrying capacity is limited by the residual 014x24 as these grains reduce the current carrying cross-section of the film and contains the elements needed for the transformation of the mixed state “4413” to Bi-2212. By annealing at 850°C, a conversion is achieved [14], [17] and j_c continues to increase with annealing time [18]. This is in good agreement with the results found in 2223 where j_c was inversely correlated with the amount of Bi-2212 intergrowths [19].

In the standard process this annealing is performed in oxygen. Hallstedt et al. [20] have shown earlier that the stability range of 014x24 strongly depends on the oxygen partial pressure in the Sr-Ca-Cu-O system. Can this fact be extended to the Bi-Sr-Ca-Cu-O system? This would be beneficial to enhance the slow and only partial dissolution of 014x24 during phase annealing at 850°C in the partial melt process. Therefore thermodynamic calculations were performed regarding the stability of 014x24 at 850°C at different oxygen partial pressures.

The one layered compound 22x1 melts about 20°C lower than Bi-2212 as DTA analysis has shown. Annealing Bi-2212 at a temperature above the melting temperature of 22x1 during the Bi-2212 phase annealing can reduce the amount of intergrowths. Thermodynamic calculations were performed regarding the stability 2201 at elevated temperatures at pO_2=1 bar.

Hasegawa et al. [9] has applied reduced oxygen partial pressures to Bi-2212 thin films during the partial melt and crystallization step achieving an increase in j_c. The aim of this experimental study is to apply the calculated thermodynamic predictions to the phase annealing step of the partial
melt process. The influence of reducing the content of residual 01424 by annealing at low pO₂ or residual 2201 by annealing at a higher temperature on the critical current density is investigated. A correlation between j_c, the microstructure and the phase composition of different processed material is aimed. Therefore, in this work Bi-2212 crystallized from the partial melt state was annealed at different pO₂ at 850°C or at 875°C in pO₂=1 bar.
4.2. Thermodynamic considerations

Calculations of BiO$_{3/2}$-Sr$_{2/3}$Ca$_{1/3}$O-CuO cross-sections at 850°C, pO$_2$=1, 0.2, 0.1 bar and 875°C, pO$_2$=1 bar were performed using the software package Thermocalc and the thermodynamic database assessed by [8] using the CALPHAD approach. From these calculations the stability ranges (multi and single phase regions) of 014x24 and 2201 are derived (FIGURE 1 and FIGURE 2). As the oxygen partial pressure decreases, the stability range of 014x24 is reduced. Note that especially changing the pO$_2$ from 0.2 to 0.1 bar results in a strong reduction of the stability area. The stability range of 2201 is only slightly reduced by decreasing pO$_2$, but can be further reduced by increasing the temperature to 875°C in pO$_2$=1 bar. Latter however leads to a slight gain of the 014x24 stability region.

![Figure 1: Traced by the solid lines is the stability range of 014x24 (multi and single phase region) at different oxygen partial pressures in the BiO$_{3/2}$-Sr$_{2/3}$Ca$_{1/3}$O-CuO system at 850°C. The area inside the dashed lines, around the Bi-2212 phase is the 4 phase region Bi-2212, 2201, 014x24 and 91150. (Calculated phase diagram using the CALPHAD approach)](image)
Figure 2: Traced by the solid lines is the stability range of 2201 (multi and single phase region) at different temperatures and oxygen partial pressures in the BiO$_{3/2}$-Sr$_{2/3}$Ca$_{1/3}$O-CuO system. The area around the Bi-2212 phase defined by the dashed lines represents the 4 phase region Bi-2212, 2201, 014x24 and 91150. (Calculated phase diagram using the CALPHAD approach)

According to thermodynamics either of the main residual phases 014x24 and 2201 can be reduced by two specific heat treatments. (a) Enhanced dissolution of 014x24 by annealing in reduced oxygen partial pressure at 850°C and (b) Dissolution of 2201 and the mixed state “4413” by annealing at 875°C.
4.3. Experimental

Samples of Bi-2212 were processed by the partial melt process. In TABLE 2 and FIGURE 3 the temperature/time schedule of the process is shown. All parameters were kept constant except the oxygen partial pressure at 850°C and the temperature at \( pO_2 = 1 \) bar during the annealing step (TABLE 2, step 4 resp. 4*). The oxygen partial pressure varied from 1, 0.5, 0.2, 0.1 and 0.05 bar by diluting the flowing oxygen with nitrogen.

<table>
<thead>
<tr>
<th>Step</th>
<th>Heating rate (^{°}/\text{min})</th>
<th>Temperature ([°C])</th>
<th>Holding time ([\text{hr}])</th>
<th>Atmosphere ([pO_2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>180 or 120</td>
<td>850</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>895</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td>850</td>
<td>2 (lag time)</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>850</td>
<td>18</td>
<td>1 - 0.1</td>
</tr>
<tr>
<td>4*</td>
<td>30</td>
<td>875</td>
<td>16</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>820</td>
<td>20</td>
<td>0.1</td>
</tr>
<tr>
<td>6</td>
<td>with furnace</td>
<td>80</td>
<td>0</td>
<td>0.1 - &quot;0&quot;</td>
</tr>
</tbody>
</table>

Table 2: Temperature and time parameters of the partial melt process corresponding to FIGURE 3.

Figure 3: Parameters of the partial melt process (partial melt state and first annealing step of the partial melt process). The full line corresponds to the standard process (4, TABLE 2), the dashed line corresponds to the sample annealed at 875°C (4*). The
double arrows indicate the quenched samples.

The powders used for the experiments were obtained from commercial sources (SBS in courtesy of Solvay, Merck in courtesy of Merck, Nex3 in courtesy of Nexans) or made in-house by calcination of oxides and carbonates (ETH VI). All powders are single phase Bi-2212 with a nominal stoichiometry of Bi:2, Sr:2, Ca:1, Cu:2 (Nexl is a uncalcined melt quenched precursor). 5 samples of each precursor were made for each experiment by uniaxially pressing (250 MPa) the precursor in an Ag crucible. The sample dimensions are 13 mm in diameter with an initial thickness of 700 \( \mu m \) and a final thickness of around 400 - 500 \( \mu m \).

The critical current density of the processed samples is measured with an AC-magnetometer, using the 10 \( \mu V/cm \) criteria (\( j_c \) is about 30% higher than measured with the 1 \( \mu V/cm \) criteria).

To study the influence of the atmosphere on the microstructure, samples were quenched during the annealing step at 850°C (step 4/4*). The states from which the samples were quenched are shown in FIGURE 3. Quenching was performed in a vertical furnace with controlled atmospheres and quenched into oil.

The phase composition of the quenched and fully processed samples were studied by powder diffraction (Siemens D5000). The samples were milled before measurement and the peak positions adjusted by an internal reference (quartz). The microstructures were analysed by SEM (Leo 1530) on polished samples and the volume content of second phases determined by the mean intercept method (Lince Software).

To study the peritectic liquid of Bi-2212 in the partial melt state at 895°C an ion etched thin section of quenched material was analysed by TEM (Phillips, CM30 300keV).
4.4. Results

4.4.1. Influence of annealing temperature and oxygen partial pressure on the critical current density

In Figure 4, the critical current density is shown versus the oxygen partial pressure during the annealing step at 850°C. Reducing $p_{O_2}$ during annealing after the crystallization at 850°C from the partial melt state leads to an increase of $j_c$ of fully processed samples. Annealing at $p_{O_2}=0.1$ bar improves $j_c$ by an average of 65% compared to samples annealed at $p_{O_2}=1$ bar. A further decrease of $p_{O_2}$ to 0.05 bar results in a re-melting of Bi-2212 at 850°C and the loss of superconductivity. Low $j_c$ will also result, if $p_{O_2}$ is reduced immediately after the crystallization or if the material is annealed at 875°C in pure oxygen. High $j_c$ are only found after a lag time of 1 to 2 hrs. annealing in oxygen after crystallization. All precursors, fully reacted and partially reacted ($N_{ext}$) show a gain of $j_c$ with decreasing $p_{O_2}$ during annealing.

![Figure 4: Critical current density in dependence of the oxygen partial pressure $p_{O_2}$ during annealing at 850°C after crystallization. The filled diamonds represent data of samples made of SBS precursor, one processed without a lag time (3, TABLE 2) and the other annealed at 875°C (4*).](image)
Chapter 5: Enhanced Residual Second Phase Dissolution by Atmosphere Control in Bi-2212 Superconductors

The results clearly show that $j_c$ increases if the material is annealed at $0.09 < pO_2 < 0.2$. According to the thermodynamic calculations this effect can be attributed to the enhanced dissolution of the $\text{O}_{14\times24}$ (FIGURE 1).

To elucidate the mechanisms that lead to this gain but also to the failure of the annealing at higher temperature, the phase composition of fully processed material as well as quenched samples during crystallization and annealing were determined by XRD.

4.4.2. Influence of temperature and $pO_2$ on the phase composition

In TABLE 3 the phase compositions of the samples quenched is listed and FIGURE 5 shows the evolution of the 2201, 22$x_1$ (006), “4413” (007) and Bi-2212 (008) reflection during processing.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Phase composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q896 2hr</td>
<td>22x1, $\text{O}_{14\times24}$, 91150 and liquid</td>
</tr>
<tr>
<td>Q855</td>
<td>2201, 22x1($x$=0.4), $\text{O}_{14\times24}$, 91150 and liquid</td>
</tr>
<tr>
<td>Q850</td>
<td>2201, “4413”, Bi-2212 and residual $\text{O}_{14\times24}$ and liquid</td>
</tr>
<tr>
<td>Q850 2hr</td>
<td>Bi-2212a, Bi-2212b, residual $\text{O}_{14\times24}$</td>
</tr>
<tr>
<td>Q Ref</td>
<td>Bi-2212 and 2201 in a mixed phase, residual $\text{O}_{14\times24}$</td>
</tr>
<tr>
<td>Q Temp</td>
<td>Bi-2212, residual $\text{O}_{14\times24}$</td>
</tr>
<tr>
<td>Q Atm</td>
<td>Bi-2212, residual $\text{O}_{14\times24}$</td>
</tr>
</tbody>
</table>

Table 3: Phase composition of samples that were processed according to FIGURE 3.
Figure 5: X-ray powder diffraction 2 theta plots (XRD) of samples quenched during annealing at 850°C in different oxygen partial pressures, temperatures and times and of fully processed material. The abbreviations correspond to FIGURE 3. (a) Quenched upon cooling down from 895°C with 45°/hr in pO2=1 bar (pure oxygen), (b) Quenched after annealing for 20 hrs. at 850°C (QRef, QAtm) and 875°C (QTemp), (c) Fully processed Bi-2212.
From TABLE 3 the evolution of the phases is as follows: In the partial melt state (Q895, 2hrs) \(014x24, 91150\), a liquid and the one layered compound 22x1 are present. In case the material is cooled down from 895 to 855°C under \(\text{pO}_2=1\) bar (Q855) the Ca-free one layered compound (2201) is formed together with 22x1 with \(x=0.4\). The latter has the composition of the melt at 895°C. In addition \(014x24, 91150\) and residual liquid is present. When cooling from the partial melt state to 850°C (Q850) instead of 855°C, the major phase is the “4413” and primary Bi-2212 and residual \(014x24, 2201, 22x1\) and melt are present. Upon further annealing at 850°C for 2hrs (Q850, 2hrs), the mixed phase “4413” disappears and Bi-2212 is the dominant phase with some residual \(014x24\). This transformation of the mixed state “4413” which consists of Bi-2212 with 2201 intergrowths to the Bi-2212 was described earlier by Heinrich [17] and was also observed by Rikel [16] when changing cooling rates during crystallization. Upon further annealing, the content of intergrowths decreases as shown in FIGURE 5b. By decreasing the oxygen partial pressure (step 4) or increasing the temperature (step 4*) the amount of “4413” can be further reduced compared to the material annealed in pure oxygen (reference material). In fully processed material (FIGURE 5c) the amount of intergrowths has further decreased, especially for the material annealed in \(\text{pO}_2=1\) bar at 850°C. Least intergrowths are found when the material is annealed at 875°C (FIGURE 5c, Temp).

During annealing the Bi-2212 phase does not only change due to less 2201 intergrowths, but also its Sr/Ca ratio changes. This is illustrated in FIGURE 6, where the normalized 0010 Bi-2212 reflections of fully processed materials are shown. The 00x reflections of Bi-2212 annealed in reduced \(\text{pO}_2\) or at higher temperature are shifted to lower angles compared to these of samples annealed in pure oxygen at 850°C.
Figure 6: Normalized 0010 reflections of fully processed Bi-2212 annealed at 850°C in $pO_2=1$ (Ref) and 0.1 bar (Atm) and at 875°C in $pO_2=1$ bar. The dashed line is of the sample annealed at $pO_2=0.2$ bar. The shift of the peak to lower angles corresponds to an increase of the c-axis from 30.84 Å (Ref) to 30.88 Å (Atm) to 30.9 Å (Temp). The abbreviations correspond to FIGURE 3.

Besides the changes of Bi-2212 during annealing, also 014x24 changes in stoichiometry. In FIGURE 7 the normalized 014x24 peaks of fully processed material are shown. Due to increasing Ca content of the phase, $x=5.4$ (Temp), 5.75 (Ref) and 5.81 (Atm) the peaks shift to higher angles.

Figure 7: 014x24 peak of fully processed Bi-2212 material annealed at 850°C in $pO_2=1$ (Ref) and 0.1 bar (Atm) and at 875°C in $pO_2=1$ bar. The shift of the peaks to lower angles corresponds to an increasing Sr content of the phase $(Sr_{14.4}Ca_xCu_{24}O_{38})$. The 014x24 phase of material annealed in $pO_2=0.1$ bar are Ca richer and Sr poorer. The abbreviations correspond to FIGURE 3.
The peak shifts observed in the 00x reflections of Bi-2212 and $^{014}_{x}^{24}$ originate from slightly different phase stoichiometries. As the starting composition of all the samples was identical these different stoichiometries can be attributed to the different “4413” conversion mechanisms. The c-axis of Bi-2212 increases mainly when: (a) Bi-2212 is oxygen deficient [21], (b) Ca is substituted by Sr [22] [23], (c) Cu content $>$ 2 atomic ratio in Bi-2212, often in combination with Sr $>$ 2 [24].

We do not attribute the shift of the peaks to the change in oxygen content in the crystal as fully processed material show this shift, despite identical annealing steps 5 and 6 (TABLE 2). Additionally annealing experiments with Bi-2212 precursors at 850°C in different partial pressures show no peak shift in this range. Points (b) to (c) are emphasized by the fact that the earth alkali Sr and Ca can substitute each other in Bi-2212 over a broad range and residual Sr and Cu are present from the “4413” and $^{014}_{x}^{24}$ decomposition.

EDX analysis of $^{014}_{x}^{24}$ only partially confirms the XRD data. The Sr/Ca ratios measured in the samples show higher Ca contents than calculated from XRD. However due to the broad XRD peaks and a further unknown reflection (2x1?) this mismatch can be explained. The Cu content of $^{014}_{x}^{24}$ of the fully processed samples Ref and Atm are Cu deficient compared to the $^{014}_{x}^{24}$ from the sample quench at 850°C after 2hrs (Q850 2hrs). Only the sample annealed of 875°C in $p_{O_2}$=1 bar (Temp) has the same amount of Cu. An unchanged Cu content means that $^{014}_{x}^{24}$ has not decomposed or been leached for Cu and Ca to convert the mixed state “4413” to Bi-2212.

The shift of the 00x reflections of Bi-2212 to smaller angles and thus larger c-axis annealed at 875°C in $p_{O_2}$=1 bar compared to Bi-2212 annealed at 850°C in $p_{O_2}$=1 bar can be explained by Sr and Cu uptake in Bi-2212 (FIGURE 6). A c-axis of 30.902 Å corresponds to a slightly Sr-rich compound. The uptake of Sr and Cu originating from the decomposition of the 2201 in “4413” is enabled by the higher annealing temperature [25]. The residual elements that could not be integrated into the existing phases form new phases. Reflections of Bi$_x$Sr$_y$O phases have been found in the quenched sample (QTemp) however not any more in fully processed (Temp). Sr and Cu can enable $^{014}_{x}^{24}$ phase growth leading to a Sr-rich compound as shown by FIGURE 7 and EDX.

Also the shift of the 00x reflections of Bi-2212 to smaller angles annealed in $p_{O_2}$=0.1 bar (also 0.2) at 850° compared to Bi-2212 annealed in $p_{O_2}$=1 bar can be explained by Sr and Cu uptake in Bi-2212. The shift is less strong and the c-axis is shorter, 30.882 Å, probably originating from a Sr
substitution by Ca of 0.055 stoichiometry per formula unit in Bi$_2$Sr$_{3-x}$Ca$_x$Cu$_2$O$_8$ ($x=1.055$). The compound is Ca richer due to the lower annealing temperature but also due to the dissolving 014x24 liberating Sr, Ca and Cu that convert “4413” to Bi-2212.

The 00x reflection of Bi-2212 annealed at 850°C in oxygen has the smallest c-axis, 30.839 Å, corresponding to a Ca substitution of 0.18 stoichiometry per formula unit ($x=1.18$). Such a large amount of substitution by Ca can only be correlated to a leaching out of Ca from 014x24 leading to higher Sr contents in this phase. EDX measurements show that the Sr/Ca ratio of 014x24 found in crystallized Bi-2212 samples annealed for 2 hrs. at 850°C is lower than of samples annealed for 20 hrs.

The analysis of XRD data regarding phase composition (FIGURE 5) and crystal composition (FIGURE 6 and 7) of material quenched during the PMP and fully processed, clearly shows the beneficial influence of a modified annealing step (TABLE 2, step 4 and 4*). The amount of 2201 intergrowths is reduced by annealing in reduced pO$_2$ as well as at higher temperatures. Depending on the annealing conditions the stoichiometry of the Bi-2212 and the residual 014x24 phase change. This indicates different mechanisms for the gain in Bi-2212 phase purity (FIGURE 5c) and will lead to the formation of different microstructures visible by SEM. From the proposed mechanisms it can be expected that by annealing in pO$_2$=1 bar at 850°C the volume content of 014x24 will stay constant as only Ca is leached out. By annealing at 875°C in pO$_2$=1 bar an increase in 014x24 volume content can be expected by decreasing the stability of 2201 and “4413” (FIGURE 2) but consequently precipitating Sr and Cu which then forms 014x24. By annealing in pO$_2$=0.1 bar at 850°C on the other hand, the amount of 014x24 is reduced by decreasing its thermodynamic stability (FIGURE 1). The Ca and Cu originating from its dissolution then initiates the conversion of the mixed state “4413” to perfect Bi-2212 by intercalcination.

As the critical current densities in Bi-2212 thick films and bulks are mainly determined by the current carrying cross section, microstructural analysis might give insight to the microstructural differences formed by the different annealing conditions.

4.4.3. Influence of temperature and pO$_2$ on microstructure and phase composition

During the crystallization of Bi-2212 upon cooling from the partial melt state and annealing, the dissolution of the peritectic phases, 91150 and 014x24 is a critical issue. Of these two high temperature phases, the 91150 phase dissolves readily during annealing as it is not visible in
microstructures of fully processed material by SEM, and only detected in small amounts by XRD. On the other hand, the \(0_{14\times24}\) phase is present in two different states in the microstructures of fully processed material. One is homogeneously distributed as small grains (5 - 10 µm) in the Bi-2212 matrix and the other is inhomogeneously distributed as large agglomerates of grains (5 to 20 µm), varying in size from 50 to several 100 µm in size. As this phase contains Ca and Cu, the dissolution of \(0_{14\times24}\) is essential for the conversion of the mixed state “4413” to intergrowth free, perfect Bi-2212.

Microstructures of different fully processed material are shown in FIGURE 8. Quantitative phase contents are shown in FIGURE 9. Focusing on the \(0_{14\times24}\) phase, which have a more globular morphology compared to their initial shape, rhombohedral rods, the microstructures differ mainly in amount, grain size distribution and morphology of the small grains. The grain size distributions of \(0_{14\times24}\) in the microstructures of material annealed in \(pO_2=1\) bar at 850°C (Ref) and at 875°C (Temp) are very broad, and the small grains have the shape of discs resulting from growing Bi-2212, slicing the long \(0_{14\times24}\) grains into pieces. The small \(0_{14\times24}\) grains found in material annealed in \(pO_2=0.1\) bar at 850°C (Atm) are globular. The bright phase mainly seen in the microstructures of the Ref material corresponds to “4413”. Its content is lowered by annealing at higher temperature as well as in reduced oxygen partial pressure.
The microstructure of fully processed Bi-2212 annealed at pO$_2$=0.1 bar at 850°C without a lag time of 2 hrs. consists of very large Bi-2212 grains (not shown here) compared to material with a lag time and explains the strong decrease of 63% in $j_c$.

Figure 8: Microstructures of fully processed samples (backscatter SEM image). The grey matrix is the Bi-2212 phase. Brighter matrix zones consist of the mixed state “4413”. The black grains are the 014x24 phase, they are present as single small grains or as large clusters. Bright grains are Ag precipitates. The abbreviations Ref, Temp, Atm correspond to fully processed samples that were annealed according to FIGURE 3.

Volume contents and the grain sizes of 014x24 evolve differently depending on the annealing conditions after Bi-2212 crystallization from the high temperature state and a lag time of 2 hrs., as shown in the microstructures of quenched and fully processed samples (FIGURE 9). In the partial melt state at 895°C, after annealing for 2 hrs. necessary for homogenisation, the material consists of around 37 vol% liquid, 36 vol% 91150 and 27vol% 014x24. As the other phases nearly completely disappear after crystallization of Bi-2212, only 014x24 is regarded for the further discussion. In samples quenched after cooling from 895 to 855°C at 45°/hr no crystallization of Bi-2212 was observed, only a slight coarsening of the 014x24 grains [16] and a minor increase in
014x24 volume content which is not understood. At 850°C Bi-2212 and 2201 crystallize in a very narrow temperature window during which volume content and grain size of the 014x24 phase decrease. After 2 hrs. annealing the volume content of the 014x24 has strongly decreased. Both the volume contents and the grain size of 014x24 develops both very differently for different annealing conditions. Annealing in reduced oxygen partial pressures (Q Atm, Atm) leads to much lower volume contents of 014x24, but the grain size is slightly larger than in material that was conventionally processed (Q Ref, Ref). The reason for the larger grain size is that only the large 014x24 grains remain in the microstructure of material annealed at pO₂=0.1 bar. Annealing at temperatures above 850°C (Q Temp, Temp) leads to significant increase in 014x24 volume content and a slight grain coarsening. The volume fraction of 014x24 however then strongly decreases in the second annealing step at 820°C and in pO₂=0.1 bar (step 5, TABLE 2). The grain size remains larger than in the other materials (Ref, Atm). No big microstructural changes occurred during the first annealing step (QRef) of Bi-2212 annealed at 850°C in pO₂=1 bar. The volume fraction and grain size of 014x24 decreased only in the second annealing step.

The strong decrease in volume content of residual 014x24 in the microstructures of material annealed in pO₂=0.1 bar at 850°C (47%, FIGURE 9) correlates with the decrease in the 014x24 stability range (40%, FIGURE 1) and the increase of the critical current density (58%, FIGURE 4) compared to material annealed at pO₂=1 bar.
Figure 9: Volume fraction and grain size evolution of $\text{014x24}$ in the microstructure of quenched and fully processed samples. The first 4 steps are the same for all samples, then annealed under different conditions corresponding to FIGURE 3.

XRD analysis of samples quenched from the partial melt state and during crystallization show strong 2212 reflections and a very slight amorphous halo indicating the presence of a solidified melt. According to the thermodynamic data, literature and own observations it is evident that there is a liquid present. As the 2201 and 2212 play an essential role in the crystallization of Bi-2212, a sample quenched from the partial melt state was analysed by TEM.

4.4.4. TEM analysis of Bi-2212 quenched from the partial melt state

FIGURE 10 is a high resolution image of quenched melt found between the solid peritectic phases of Bi-2212 quenched from 895°C into oil and the diffraction pattern thereof. Nano-crystals of 20 - 25 nm are found in an amorphous matrix. The diffraction pattern consists of an amorphous ring of the quenched melt and the pattern of the one layered compound 2201. The 2201 nano-crystals are believed to form during quenching, for their arrangement and the intensity of the 2201 peaks in XRD measurements decrease if the samples are splat quenched on Cu, but are not fully eliminated! This indicates that 2201 is the first phase to form upon cooling from the partial melt state and that it could act as a nucleation site for Bi-2212, which crystalizes very rapidly at temperatures around 850°C.
Figure 10: High resolution TEM micrograph of the melt of Bi-2212 quenched from 895°C into oil. 2201 nanocrystals are found in an amorphous matrix. The diffraction picture indicates the presence of an amorphous (ring) and a crystalline phase.
4.5. Discussion

Annealing Bi-2212 after crystallization from the partial melt state at reduced oxygen partial pressure or at elevated temperature (875°C) result in a reduction of the mixed state “4413” and 2201 phase as expected by the calculated phase diagrams (FIGURE 1, FIGURE 2). The mechanisms leading to this reduction however are completely different for the two different processing routes (reduced pO₂ and elevated temperature) and also result in different current carrying properties of the material.

4.5.1. Crystallization of Bi-2212 from the melt

Upon cooling down from the partial melt state (895°C) the precipitation of Bi-2212 only takes place at 850°C (45°/hr). This pronounced large undercooling of over 40°C indicates that 2201 and 2212 nucleates homogeneously [3][26][27]. As 2201 was even found in material quenched at very high cooling rates (Cu splat) it can be expected that 2201 is the first compound to crystallize and probably also acts as a nucleation site for Bi-2212, due to its structural similarity to Bi-2212. The strong (006) reflections of 2201 found in the sample quenched at 855°C (FIGURE 5a) originates from 2201 nano-crystals. Another 1 layered compound, the 22x1 is found in XRD with the composition of the residual melt that crystallized during quenching, besides the 2201 nano-crystals. At 850°C when the crystallization of 2201, “4413” and Bi-2212 has partially taken place, some residual liquid is still present [13]. This residual liquid has several consequences for the further processing: (a) The rapid decrease in grain size and volume content of 014x24 during the first 2 hrs. of the annealing step at 850°C is attributed to the residual liquid in the material, enabling rapid diffusion. After the melt has completely reacted the 014x24 volume content of samples annealed in pO₂=1 bar do not further decrease. (b) The immediate reduction of the pO₂ to 0.1 bar after cooling down to 850°C leads also to a reduction of the stability range of 2201 (FIGURE 2) thus lowering the amount of 2201 nano-crystals or nuclei for the Bi-2212 phase formation. Consequently the number of Bi-2212 grains are less and they grow larger. This is not a benefit as the low jₑ show, then a percolating current pathway through this non-textured polycrystalline material is more feasible in fine grained material. (c) The peritectic decomposition temperature is decreased when the oxygen partial pressure is lowered [9]. As Bi-2212 requires a high undercooling rate for nucleation and growth from the melt, changing pO₂ before the major crystallization has the same effect as increasing the temperature. This has a drastic influence on the crystallization. (d) For the dissolution reaction between 014x24 and the melt at 850°C and the consequent crystallization of Bi-2212, oxygen is needed. The oxygen will initially diffuse through
the melt and then later through Bi-2212 grains. The latter is slower than the first process. Therefore especially during the final state of crystallization of Bi-2212 a large chemical gradient between the inner of the sample and the surrounding atmosphere is essential [3].

Consequence (b) - (d) explain the necessity of a lag time before reducing the oxygen partial pressure. This is confirmed by the very low critical current densities (FIGURE 4, data point bottom left) and the large Bi-2212 ribbons found in material without the lag time of 2 hrs.

4.5.2. Microstructure formation during annealing

Depending on the annealing conditions (FIGURE 3) after the lag time, different microstructures and critical current densities result:

**Annealing in \(pO_2=1\) bar at 850°C:** The negligible differences in microstructure and phase composition of material annealed for 2 and 20 hrs. (unchanged 007 peaks of the “4413” phase in FIGURE 5a and b and the invariant 014x24 volume content in FIGURE 9) suggest that the material is in a local equilibrium. All further changes of microstructure and phase content take place only during the second annealing step at 820°C with a pO2 of 0.1 bar and some of the small disc like 014x24 grains are dissolved, enabling the transformation of “4413” to Bi-2212.

**Annealing in \(pO_2=1\) bar at 875°C:** The strong increase of 014x24 phase content can be attributed to its enhanced stability (FIGURE 9) at higher temperatures but mainly to the decomposition of “4413” to Bi-2212 and Bi, Sr and Cu, as 2201 is less stable (FIGURE 5 and FIGURE 2). These elements then form Bi\(_2\)Sr\(_y\)O compounds and 014x24. During the second annealing step at 820°C in pO2=0.1 bar these phases then react to Bi-2212. This is supported by the fact that similar phase contents of 014x24 are found in fully processed material of latter and conventionally (Ref) processed. The increased grain size can be attributed to Ostwald ripening.

**Annealing in \(pO_2=0.1\) bar at 850°C:** The driving force for all the changes is the enhanced dissolution of the 014x24 phase by decreasing its stability range (FIGURE 1). Its dissolution releases Sr, Ca and Cu. This has 2 consequences on the microstructure formation and consequently on the \(j_c\) of the material: (a) Reduction of the 014x24 phase content (FIGURE 7) makes space for growing Bi-2212, thus increasing the current carrying cross-section. (b) Conversion of the mixed state “4413” by inter-calcination of Ca and Cu, leading to perfect Bi-2212 (FIGURE 5b) and therefore more Bi-2212.
4.5.3. Critical current densities

The comparison of the critical current densities of conventionally processed Bi-2212 bulk material (Ref sample) and material obtained by varying pO$_2$ and temperature during annealing can be summarized as follows: (a) The critical current density of fully processed Bi-2212 bulk material is increased if the material is annealed in reduced oxygen partial pressures (pO$_2$=0.2 to 0.1 bar) after crystallization at 850°C. This gain of j$_c$ can be explained by the enhanced dissolution of Bi$_2$O$_{24}$ during annealing, transforming “4413” to perfect Bi-2212. Dissolution, transformation and formation of new Bi-2212 lead to a higher current carrying cross-section. Reducing the pO$_2$ too low (<0.1 bar) results however to the decomposition of Bi-2212 at 850°C. (b) The non-linear increase of j$_c$ with decreasing pO$_2$ goes parallel to the stability range of Bi$_2$O$_{24}$ (Figure 1) and its dissolution in the microstructure. The pO$_2$ is limited to 0.1 bar at 850°C because of Bi-2212 remelting. (c) Increasing the annealing temperature does not result in higher critical current density, although the amount of mixed state “4413” and 2201 is reduced.

These facts indicate that the increase in j$_c$ can be attributed to the increased current carrying cross section assigned to the reduced Bi$_2$O$_{24}$ phase content and subsequently in increased Bi-2212 volume contents with correct stoichiometry and grain size and not to the reduced amount of mixed state “4413” and 2201.
4.6. Conclusions

The mixed state "4413", 2201 and residual 014x24 are the second phases found in the microstructure of partial melt processed Bi-2212. High amounts of these phases remain in the final microstructures of a typically processed Bi-2212, limiting the critical current density (j_c). In this work, these phases were significantly reduced by applying a modified post annealing, resulting in enhanced phase purity of Bi-2212, and subsequent j_c increase by up to 65%.

Microstructure study suggests that 2201 is probably the first phase to form during cooling down from the partial melt state and subsequently serves as the heterogeneous nucleation site for the crystallization of Bi-2212. Reducing the stability of the nuclei will lead to large Bi-2212 grains and low j_c in non-textured bulk material.

Post annealing at high temperatures, e.g. 875°C in pO_2=1 bar results in reduced "4413" and 2201 contents, without leading to j_c improvement. On the contrary, post annealing at 850°C in reduced pO_2 is accompanied with a reduction in 014x24 content, believed to be caused by the reduced 014x24 stability range and enhanced by liquid assisted diffusion. The calculated phase diagrams predicted the reduced stability ranges in dependence of the annealing conditions.

The enhanced dissolution of 014x24, typically distributed as isolated grains and in clusters, accounts for the observed 77 K, self-field high j_c of 6000 A/cm^2, the highest reported for non-textured bulk Bi-2212.

Such significant j_c improvement can be attributed to increased effective current carrying cross-section, gained directly as a result of reduced 014x24 cross-section and indirectly from the transformed mixed state "4413" to Bi-2212 after incorporation of the elements released from the dissolved 014x24.

The current work confirms that post annealing optimization is a promising method to further improve j_c. However only the reduction of the large 014x24 agglomerates in the microstructures will lead to further significant increase in j_c. Study on the formation of 014x24 and these agglomerates could hold the key for novel processing pathways.

It is further speculated that major j_c improvement can be expected from the other HTS compounds, like Bi-2223 and Y-123 by re-studying their critical processing steps, such as decomposition and crystallization.
Chapter 5: Enhanced Residual Second Phase Dissolution by Atmosphere Control in Bi-2212 Superconductors

References

Outlook

One of the main outcomes of this work is that all the major changes in the material during processing, the peritectic decomposition of the precursors to the high temperature state and the crystallization of Bi-2212 from the melt, are nucleated. In both cases a certain nuclei density is required so that the material can "homogeneously" transform from one state to the another, from solid powder to the partial melt state and back to the solid state. If the nuclei density in the precursor is too low then it will decompose inhomogeneously resulting in an inhomogeneous partial molten state. In case the nuclei density in the melt is too low then the Bi-2212 grains will grow to very large ribbons making the formation of a percolating network of grains through the material more difficult. Both consequences will lead to processed components with low critical current densities $J_c$.

Further optimization of the precursors and partial melt process to increase $J_c$ should be done under the aspect to maximize the homogeneity of the microstructures at all stages of the partial melt process. This can be done by providing sufficient nucleation sites for the material phase transformations as discussed above.

X.1. Future precursor development

This work has shown that large second phases (Chapter 1 and 2) in the precursor, melt formation during calcination and high calcination temperatures (Chapter 3) have a deteriorate effect on the critical current density $J_c$ of partial melt processed material. It was found that precursors that are not of Bi-2212 phase composition and can retain 2201 and Bi-2212 formation to high temperatures yield components with high $J_c$ (Chapter 4). The latter results can be explained from the aspect of reducing the nuclei density for the peritectic decomposition by forming large and perfect Bi-2212 platelets. The effect of the precursor on $J_c$ is to provide a homogeneous partial melt state in which the peritectic phases are small, their particle size distribution is narrow and they are evenly partitioned. To reach this goal the precursors need to be further optimized. Several approaches are proposed like (a) In-situ calcination of unreacted starting material during partial melt processing. The mixture of starting elements is processed to a green body and is reacted during heating to the partial melt state. The parameters for heating the unreacted components have to be adapted to the nature and particle size of the starting material. (b) Introduction of heterogeneous nuclei for the peritectic decomposition. These can be Ag particles, material quenched from high
temperatures and low melting phases like Bi$_2$CuO$_4$ or 22x1. Latter phases would have to be completed to the Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry by a further precursor as described in chapter 4. An experimental approach would be to mix these potential nuclei in different amounts to a fully reacted Bi-2212 precursor and study the effect on the partial melt state and $j_c$ of the processed components. (c) Adjusting the reactivity of the two or multi-phase precursor to Bi-2212 by the particle size of the phases. An experiment could be done for example with “SP 014x24+Co” (chapter 4) varying the particle size of 014x24. (d) Adjusting the reactivity of the two compound precursor 22x1 and 01x1 by changing the Sr and Ca content in the phases. This work shows that precursors with the Ca free 2201 phase yields fully processed components with low $j_c$, whereas with the 22x1 with a Ca content of x=0.4 components with the highest $j_c$ were achieved. In the Bi-Sr-Ca-Cu-O system the melting temperature of many phases decreases with increasing Ca content. Calculations of the isothermal cross-section (Bi$_{0.5}$Sr$_{2/3}$Ca$_{1/3}$O-CuO) at 850°C in oxygen show that with increasing Ca content (Bi$_{1.5}$Sr$_{1/2}$Ca$_{1/2}$O-CuO) the area of the melt single phase area increases.

X.2. Future partial melt process optimization

In chapter 5 the low critical current densities $j_c$ of the samples that were annealed at 850°C at reduced p$_{O_2}$ without a lag time of 2 hrs after crystallization of Bi-2212 from the partial melt state were explained by the destruction of nuclei for further Bi-2212 crystallization in the solidifying material. This explanation was drawn after the microstructures consisted of large Bi-2212 ribbons and the calculations had shown that the stability of 2201, (the Bi-2212 nuclei) is reduced with decreasing oxygen partial pressure p$_{O_2}$. From this result we conclude that the formation of a high density of percolating networks of Bi-2212 grains in the material cannot be established by too large Bi-2212 grains (ribbons). This is also supported by results from ABB where an increase of $j_c$ was observed up to a cooling rate of 45°/hr during Bi-2212 crystallization from the partial melt state. By applying different cooling rates the Bi-2212 grain size can be adjusted as recent experiments have shown. The latter experiments, which will be published soon, also show that the nuclei density can be influenced by the maximum temperatures during the partial melt state. This gives us two parameters with which we can reduce the nuclei density of the partial molten material, the maximum temperature and the p$_{O_2}$. Are there also possibilities to increase the nuclei density? The following approaches are proposed: (a) Study the influence of slightly reduced p$_{O_2}$ during the partial melt state on $j_c$ of fully processed material and the Bi-2212 grain size. (b) Study the influence of a two or more step cooling from the high temperature state, once promoting the formation of
nuclei, then their growth to Bi-2212. (c) The annealing temperature of 850°C has been used after the crystallization of Bi-2212 in this work. Previous work of Buhl, Lang and ABB have shown that highest $j_c$ are achievable when annealing in oxygen at this temperature. However this temperature also becomes a variable when the $pO_2$ is varied. An experiment could be the cyclic variation of temperature and $pO_2$ but avoiding a re-melting of Bi-2212. (d) Study the influence of gas flow during partial melt processing. It seems that a certain gas flow is required, especially during the high temperature state in order to get components with high $j_c$. It could be that a very slight temperature gradient is of benefit during Bi-2212 processing.
Appendix 1: Starting powder, Precursor and Processing Specifications

Starting Powder, Precursor and Processing Specifications

1.1. Starting oxides and carbonates

The experiments regarding phase and precursor preparation was done with Bi₂O₃, SrCO₃, CaCO₃ and CuO as starting material. These starting oxides and carbonates were purchased from ABB Corporate Research in Baden-Dättwil (M. Hoidis) and were originally produced by Solvay Barium Strontium in Germany or for Bi₂O₃ by Pharmacie Centrale de France.

<table>
<thead>
<tr>
<th>Element</th>
<th>Particle size [µm]</th>
<th>Purity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₂O₃</td>
<td>6.77</td>
<td>99.98</td>
</tr>
<tr>
<td>SrCO₃</td>
<td>0.95</td>
<td>99.98</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>1.64</td>
<td>99.98</td>
</tr>
<tr>
<td>CuO</td>
<td>4.37</td>
<td>99.98</td>
</tr>
</tbody>
</table>

1.2. Reference Bi-2212 precursor

As a reference to all the experiments of this work the fully reacted stoichiometric Bi-2212 precursor of Solvay (SBS) was used. This precursor was chosen as our industry partner ABB Corporate Research applies this precursor for the production of their fault current limiter components. ABB decided to use the precursor of Solvay because components partial melt processed from it showed the highest critical current densities \( J_c \), compared to the other commercial producers like Merck, Nexans and Praxair.

The Solvay precursor was purchased from ABB and originates from the SLB 20 series, Lot 1538/320-1.

1.3. Substrate material

As substrate material for the partial melt process, Ag foils with a thickness of 100 µm was used. Samples were produced by pressing the precursor into crucibles made from Ag foil.
Appendix 1: Starting powder, Precursor and Processing Specifications

A1.4. Furnace

All the samples were partial melt processed at ABB Corporate Research in Baden-Dättwil. The samples were placed on a MgO coated stainless steel plate and then placed into a stainless steel box with the dimensions of L30 x B20 x H10 cm as shown in FIGURE 1. This box was placed into a conventional furnace (Solo Switzerland, 117-23/13/40) with the inner dimensions of L40 x B24 x H15 cm.

![Diagram of furnace setup](image)

FIGURE 1: Set up in which the samples were partial melt processed.

A1.5. Atmosphere control during partial melt processing

The atmosphere in the box was controlled by blowing 100 l/hr of pure oxygen, nitrogen or mixtures of both through the gas inlet. The purity of the gases corresponded to technical gas. The results showed that the critical current density \( j_c \) of the fully processed material is very sensitive to the gas flow. This is considered as the reason for different results when processing Bi-2212 with high \( j_c \) at ETH despite a much superior furnace regarding temperature homogeneity.

A1.6. Measurement of the critical current density

The critical current density \( j_c \) of the partial melt processed Bi-2212 samples was measured with an AC-magnetometer at ABB Corporate Research in Baden-Dättwil. An AC-magnetometer measures the magnetic response of a superconductor to an alternating external magnetic field which originates from a current that was induced in the superconductor. Using the Bean model, \( j_c \) can be calculated. The magnetometer of ABB was made in-house and consists of two separate coil with pick-up coils inside that are placed in separate cryostats filled with liquid nitrogen (77K). The coils are serially connected to an amplifier (Crown Macro-Tech 2400W) which is driven by a wave generator (sinusoidal wave, 4 Hz and 0.15V). The pick-up coils are connected inverse parallel, so
that the induced field from the coils is eliminated. The measured voltage of the pick-up coils therefore originates only from the superconductor sample. In an alternating external field this voltage corresponds to a sinusoidal wave. The maximum values can then be transformed to a critical current density by dividing this value by the sample geometry ($J_c = \text{Const.} \cdot \frac{\text{Voltage}}{\text{Sample radius}^3 \cdot \text{sample thickness}}$). The Bean model only considers currents on the sample surface.
Appendix 1: Starting powder, Precursor and Processing Specifications
Appendix 2

Preparation of Homogeneous Starting Powder Mixtures for Bi-2212 Precursor Production

The results of this work show that a precursor that will yield components with high critical current densities $J_c$ have to be homogeneous and stay homogeneous up to the peritectic decomposition at 892°C. The prerequisite of such a precursor is a homogeneous mixture of the starting elements, fine starting material (especially the carbonates, Appendix 1) and appropriate calcination parameters (Chapter 3 and 4). To get a homogeneous mixture of the starting compounds turned out to be quite an obstacles, as $J_c$ of Bi-2212 components is very sensitive to the stoichiometry and impurity elements originating from intensive milling. Further it was unknown on what length scale mixing is necessary, atomic-, nm- or μm-scale mixing in order to get a reactive and homogeneous precursor.

In this appendix a summary of the benefits and drawbacks of several applied mixing and milling techniques is given and the technique is presented with which we finally succeeded to make precursors that yield very high $J_c$.

As starting powders oxides and carbonates were used (Appendix 1). For the co-precipitation and nitrate mixing experiments, nitrates and nitrate solutions were processed by the reaction of these oxides and carbonates with nitric acid.

One of the conclusions of this work is that calcination and partial melt processing rather promote inhomogeneity introduced by the initial mixture of the starting compounds than reducing them. From the calcination products, then samples were partial melt processed to Bi-2212 material and $J_c$ measured. The results showed that besides homogeneous mixing it is absolutely crucial to maintain the stoichiometry and to avoid poisoning by impurity elements introduced during milling processes.
A2.1. Attrition and planetary milling

Attrition and planetary milling of the starting oxides and carbonates leads to fine and homogeneous mixtures. However a demixing can occur by sedimentation of Bi and Cu oxide, due to their high specific gravity during the drying of the slurry and the contamination from the milling agents is very high. Therefore precursors produced with this approach did not yield high \( J_c \). To quantify the influence of impurities on \( J_c \), the reference Bi-2212 precursor was poisoned purposely by several elements at very low extents so the elements could be incorporated into the Bi-2212 phase and do not form additional secondary phases. The Bi-2212 material processed from these precursors show a decrease in \( J_c \) for elements that are incorporated on Cu sites in the crystal even at very low contents.

A2.2. Mixing of nitrates

As nitrates have low melting temperatures (100 - 200°C) they can be mixed on a molecular level by melting and ensuing conventional stirring of the melt. Upon increasing the temperature the nitrates then decompose and a homogeneous mixture is achieved. The major drawbacks of this approach is the maintenance of the stoichiometry, as nitrates are very hydrophilic and take up water from the atmosphere and the nitride decomposition releasing harmful nitroxy gases that are also responsible for boiling retardation in the increasingly viscous melt. Latter two issues and the higher costs of starting compounds compared to oxides and carbonates hinder a possible up-scaling to an industrial scale. Nitrates of the starting elements were mixed by melting and stirring and then slowly decomposed and burnt out. Fine precursors were achieved with Bi-2212 stoichiometry but the Bi-2212 material obtained after processing was very porous and not superconducting. Therefore this method was no longer applied.

A2.3. Co-precipitation

Co-precipitation is a common manner applied to achieve mixing on an atomic or molecular scale. Several precursors can be purchased produced via this route. The problem of co-precipitation is the adjustment of the desired stoichiometry. As the elements of Bi-2212 have completely different solubility limits in H\(_2\)O, ranging from the very low solubility of Bi to the very high solubility of Sr in aqueous solutions a simultaneous precipitation under maintenance of the stoichiometry is difficult. These problems have been overcome by precipitating the elements as carbonates and hydroxides or metal-organic complexes.
Appendix 2: Preparation of Homogeneous Starting Powder Mixtures for Bi-2212 Precursor Production

Several precursors were produced by oxalate co- and sequential precipitation. Precursors were made consisting of particles made by precipitating the different elements sequentially. The benefit of this approach was that during the precipitation of each element it was possible to adjust the optimal precipitation condition. By this sequential precipitation approach, precursors of different reactivity were made, as the elements Bi and Cu could be separated by intermediate layers of Ca and Sr oxalate. The results however did not match with the efforts made to produce the precursors as the $j_c$ of the processed material thereof were generally low.

A2.4. Ball milling

The starting compounds were mixed in parts to get Bi:2, Sr:2, Ca:1, Cu:2 stoichiometry and ball milled in butylacetate (Fluka, purum) as a solvent with 1-2 wt% Span 80 (Fluka) as a dispersion agent. After gentle ball milling in plastic jars with ZrO$_2$ balls for 2 days, the solvent was slowly evaporated while milling to avoid sedimentation. The dispersion agent was slowly burnt out in a large glass container at 350°C for 24 hrs. No Zr impurities were detected by EDX in the final dry mixture. A homogeneous mixture on the scale of the starting compounds was obtained. Starting compound agglomerates were broken up and phase separation by sedimentation was avoided.

Calcination experiments were performed in silver trays. The starting material was loosely spread in batches of 15 - 20 g in the trays. The packing height varied between 10 - 20 mm corresponding to a packing density of 1 g/cm$^3$. After calcination the precursors were milled in an achat mortar and pistil by hand and sieved (63 μm).

This simple, flexible and non poisoning mixing process was the key to all further precursor experiments. It was applied to produce initial mixtures for all experiments regarding $j_c$ dependence of calcination conditions (Chapter 3) and of phase composition (Chapter 4).

A2.5. Conclusions of mixing and milling

These results put up different requirements, partially contradicting ones, on precursor production yielding high $j_c$ material: (a) The processing parameters, especially $T_{max}$ and thus $j_c$ is very sensitive to the stoichiometry of Bi-2212 (Chapter 1). Therefore methods like solid state reaction or melt mixing are favoured over chemical mixing routes like co-precipitation. (b) Homogeneous mixing of the starting material is essential to avoid second phase formation and low temperature melts. (c) The amount of carbon introduced in the precursor by processing should be minimal and of a nature that is easy to burn out. (d) The atmosphere exchange during calcination
should be high to avoid high CO$_2$ partial pressures in the precursor promoting melt formation leading to local phase separation, besides preventing carbon burnout and carbonate decomposition (Chapter 3). (e) The calcination temperatures should be as low as possible to avoid particle coarsening, particles with high aspect ratios, growth of second phases and the curing of material imperfections which act as nucleation sites during the peritectic decomposition (Chapter 3 and 4).

A2.6. Calcination and hydrothermal processing

After mixing of the starting compounds a heat treatment is always needed to decompose the starting compounds and to react them to the desired phase composition. For the Bi-2212 phase formation temperatures above 800°C are required independently in which molecular state the starting elements are present. As this is 30°C higher than the temperature of the lowest eutectic in the Bi-Sr-Ca-Cu-O system, the formation of melt during calcination is possible. An alternative to calcination is hydrothermal synthesis of crystalline phases from an aqueous solution at high vapour pressures and temperatures just around 200°C. Many natural minerals are formed in hydrothermal conditions, for instance in volcanic zones. Quartz crystals or clays are typical examples for this synthesis. It is also applied for the synthesis of several technical chemicals like zirconia, barium titanate and Tl-2212.

For the synthesis of Bi-2212 under hydrothermal conditions a carbonate and organic ligand free precipitate is required. As the stability of the carbonates is too high and do not decompose under hydrothermal conditions and organic ligands from a conventional co-precipitation hinder the hydrothermal crystallization, Sr and Ca were precipitated as peroxides (Sr/CaO$_2$), that are highly insoluble compared to the hydroxides (Sr/Ca(OH)$_2$). Precipitating these peroxide together with the pH shift for Bi and Cu, a carbonate and carbon free co-precipitated gel was achieved. This process is, however, not trivial as Bi and Cu catalytically decompose peroxides.

The hydroxide-peroxide gel was transferred to a hydrothermal processing cell and heated for 48 hrs at 200°C. The precursors obtained after the synthesis were very fine Bi$_2$CuO$_4$, SrCO$_3$ and CuO containing mixtures. The Bi-2212 material processed from this precursor by the standard process was not superconducting. Therefore all further processing in this thesis was done by conventional heating of the unreacted oxide and carbonate mixtures. After carefully burning out of the organic, as described above, the unreacted mixtures were heated with a heating rate of 180°/hr to 550°C and then with 60°/hr to the final calcination temperature. A detailed study of the calcination parameters is presented in Chapter 4.
Appendix 3

Influence of Impurity Elements in the Precursor on the Critical Current Density of Partial Melt Processed Bi-2212

A3.1. Introduction

This appendix is an extension of Chapter 1. The properties of several commercial precursors and the critical current densities $J_c$ of partial melt processed samples were compared. The results show that precursors of same stoichiometry and phase composition yield fully processed material with different $J_c$. Reasons for this can be found in the different homogeneity, particle aspect ratio and purity of the precursors, as large inhomogeneities will lead to a reduction of the current carrying cross-section and thus $J_c$ of the final product. Unfortunately both inhomogeneity, particle aspect ratio and low amounts of impurities are hard to quantify or to detect with standard precursor characterization methods.

The arguments of nuclei density and aspect ratio regarding the homogeneity of the peritectic decomposition can be applied for precursors that were produced under the same conditions as this is the case for Nexans and Merck precursors. However the much lower $J_c$ achieved with the processed samples of the precursors SCC and PA cannot be explained by these arguments, despite particle sizes, second phase contents and melting behaviour that are very similar to the other precursors studied. It is much more probable that these precursors are poisoned by low amounts of impurity elements, as shown in the following section.

To study the influence of impurity elements, a SBS precursor was deliberately contaminated at low levels with impurities that originate from the starting oxides and carbonates and during precursor handling and processing.
A3.2. Experimental

The impurities added to the precursors are either elements that can be found in the starting powder or originate from precursor processing. Elements chemically similar to the elements of the starting powder are Ni and Zn for Cu, Pb for Bi and Na for Ca. The impurities originating from precursor processing were Zr, Mg and Al from milling equipment and Fe and Ni from stirrers and mixers.

Depending on the occupation site of the impurity atom in the Bi-2212 lattice, 0.5 and 1 at% were added related to the initial atom of the Bi-2212 crystal. Elements occupying the Ca site are therefore added in half the amount compared to elements aiming the Cu, Sr or Bi site due to the stoichiometry of Bi2, Sr:2, Ca:1, Cu:2. Elements preferably occupying the Cu site are Fe, Ni, Zn. The Bi site is preferred by Pb and the Ca site by Na, Al, and probably also by Zr and Mg.

Nitrates of the impurity elements were dissolved in water and mixed with the SBS precursor by an ultrasound treatment. To investigate the influence of this treatment, unpoisoned SBS was treated as the poisoned material and then processed. XRD and SEM/EDX analysis were preformed on the processed samples.

A3.3. Results

When processing precursors, either during production of the starting material or later, during production of the precursor, the probability of contaminating the material with foreign elements is high. Impurity atoms of any kind influence the superconducting properties of Bi-2212. The majority of data is available on the critical temperature ($T_c$) and critical magnetic field ($H_{irr}$). However little is known about the influence of impurity elements on the critical current density ($J_c$) of fully processed material.

The amount of impurity elements added is chosen between 0.5 and 1 at% so that no impurity rich second phases will form. Depending on the potential occupation site of the impurity atom in the Bi-2212 lattice, 0.5 and 1 at% of impurities were added related to the initial Bi-2212 material.

The $J_c$ is very sensitive to impurity elements as shown in FIGURE 1. The mixing treatment leads to 10% lower $J_c$ for the unpoisoned SBS precursor. At impurity contents of 1 at% all the $J_c$ are reduced except for Na, Mg and Zr. At lower impurity levels an increase of $J_c$ is found for Na, Pb, Al,
Mg and Zr. The elements Ni, Fe and Zn led to a decrease of $j_c$ also in low concentrations. XRD patterns, SEM images and EDX measurements do not show any second phases or structural changes of Bi-2212.

Figure 1: Influence of starting powder impurities (a) and processing impurities (b) on the critical current density $j_c$.

From literature several effects of the impurity (doping) elements are summarized:

_Sites occupied by the impurity elements:_ Cu sites are occupied by Fe, Ni, Zn [2], [7] and Al [3], Ca sites by Na [3], [13] and Bi sites are occupied by Pb [8]. No data was found for Zr and Mg.

_Effect of impurity elements on $T_c$: _The transition metals Fe, Ni, Zn [7] and Al [3] reduce $T_c$, whereas it is increased by Na doping [5]. No data was available on the elements Zr, Mg and Pb.

_Effect of impurity elements on the melting of Bi-2212:_ Na and Pb doping decreases the melting point of Bi-2212 [9], [6], [4].

_Effect of impurity elements on $j_c$: _Noetzel et al. [7] report that low concentrations of Fe (0.6 at%) and Ni (0.9 at%) increase $j_c$ at $T/T_c \geq 0.1$. For Pb doping an increase in $j_c$ has been reported by various authors [1], [10], [11]. An increase in $j_c$ was also found in Mg doped material at 4.2 K [12]. For the other elements no data was found.
The results show that: (a) Impurity elements that go on Cu places such as Fe, Ni, Zn and Al have a strong deteriorating influence on \( J_c \) at 77 K, also in low concentrations, which is in contradiction to [7]. This is reasonable as the superconductivity takes place in the Cu-O layers. These elements must be avoided in starting powders as well as during processing. (b) In low amounts the elements Zr, Mg, Na, Pb and Al lead to an increase of \( J_c \) at 77 K. Very often this positive effect can be attributed to enhanced pinning of the material or an increase in \( T_c \) as for Na [5]. The positive effect of Al at very low concentrations can have 2 reasons [3], either at these concentrations \( T_c \) is not decreased or Al does not yet substitute Cu sites.

A3.4. Conclusions

The results show that impurity elements have a strong influence on \( J_c \) already in low concentrations. It was found that elements substituting the Cu site like Ni, Fe and Zn strongly reduce \( J_c \) even at contents as low as 0.5 at%. A common sources for contamination during precursor production and processing is milling. Therefore the calcination should be done with homogeneously mixed starting powders, loosely spread in open crucibles in a well ventilated furnace and at low temperatures. These precautions allow the amount of milling to be minimized.
Appendix 3: Influence of Impurity Elements in the Precursor on the Jc of Partial Melt Processed Bi-2212

References


Appendix 3: Influence of Impurity Elements in the Precursor on the Jc of Partial Melt Processed Bi-2212
Acknowledgment

I want to thank my advisor Prof. L. J. Gauckler for giving me the opportunity and confidence to realize this thesis in his laboratory. His way of guidance forced me to be independent, initiative, creative and self critical - which was not always easy, but enabled a very valuable personal development. Finally when things seemed to get out of hand, he was always there with his experience, some idea or someone that could help. I also want to thank him for his patience and consequence, urging me structure thoughts to realizable projects, speech and word to comprehensible presentations and papers. His way of financial planning allowed me to focus on my research and present my results at international conferences.

I want to thank my advisor Dr. M. Chen for giving me the possibility to work at ABB Corporate Research. The scientific and non-scientific discussions we had were of great value for this work and for myself. Unfortunately this deep cooperation only found itself in the second half of this PhD, which then however lead to the very nice results and useful knowledge about Bi-2212 superconductors.

I want to thank Prof. N. Spencer for his advice during this work and for being co-examiner.

Further I want to thank the following people:

- Dr. B. Hallstedt for his advice and help dealing with the 56 solid phases and liquids of the system Bi-Sr-Ca-Cu-Ag-O. According to his calculated phase diagrams it was possible to gain insight and understanding in the decomposition and crystallization of the Bi-2212 phase.

- Dr. L. P. Meier for his advice and help in the preparation of homogeneous mixtures of starting materials. His efforts lead to a simple and effective mixing procedure enabling the production of novel precursors.

- I. Urbanek for taking care about all the financial-administrative concerns during my project and P. Kocher for technical and software support.

- A-C Risold for the preparation and TEM analysis of peritectically decomposed Bi-2212.
- My students: T. Ledermann for establishing a polishing technique of processed and quenched samples, C. Langhammer for working on mixing techniques and novel precursors, A. Vuillemier for exploring the depths of chemical precipitation techniques, G. Allidi for studying the omnipresent 221 phase regarding phase transformations, processing and texture formation, M. Koch for studying the phase purity of Bi-2212 during annealing during calcination and T. Blättler for introducing me into Bi-2212 processing at ABB.

- The former superconductor group, D. Schneider and S. Köbel for their advice, motivation and support to get this PhD started.

- The co-workers from the laboratory, for their support, discussions, humour and the many laughs, that can be so relieving when the pressure of work is high.

- The people von ABB Corporate Research, W. Paul, M. Aplanalp, M. Hoidis, P. Unternährer and the exchange students for their advice and help regarding sample preparation and processing.

- KTI Switzerland for funding this work.

My highest appreciation is addressed to my parents, who’s patience, support and constant efforts have made it possible that I was able to study and do this PhD.

Finally I want to thank my wonderful Laura for listening to my problems, sharing my sorrows, motivating me to go on and bringing so much joy into my life.
Curriculum Vitae

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Personal
Date and place of birth: 21 April 1973 in Bern, Switzerland
Nationality: Swiss
Marital status: Single

Education
   Diploma thesis: “Grain refinement in super duplex steels by thermal and thermomechnical treatment”. The work was performed at the Institute of Metals (ETHZ) and at the Laboratoire de Métallurgie Mécanique, Ecole Polytechnique Fédéral in Lausanne (EPFL).
   Semester thesis: “Rapid sintering of PMN-PT relaxor ferroelectrics by microwave radiation”. The work was performed at the National Key State Laboratory of New Ceramics and Fine Processing, Tsinghua University Beijing, China.
1990 - 1994: Matura C, Kantonsschule Aarau

Languages
• German: Mother tongue
• English: Written and spoken fluently
• French: Spoken skills better than written

Extracurricular activities
Music: During my years as a student I played in the ETH Big Band, with concerts in Switzerland, Germany and France. Due to lack of time I can no longer perform this hobby.
Professional career

1999 - present: Ph. D. student at the Institute of Nonmetallic Inorganic Materials, Materials Departement, Swiss Federal Institute of Technology in Zurich (ETHZ). My supervisors were Prof. Ludwig J. Gauckler and Dr. Makan Chen (ABB Corporate Research).

This work was done in co-operation with ABB Switzerland Corporate Research, Baden Dättwil. The aim is to increase the critical current density of Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_8$ high temperature superconductor thick films used in fault current limiters. An increase by a factor of 2.4 could be achieved by application of novel precursors and processing parameters.

Supervisor of 5 semester thesis.


*Diploma thesis:* The aim of the work was to improve the mechanical properties of super duplex stainless steels. It was achieved by grain refinement induced from thermal and thermomechnical treatment. The work was performed at the Institute of Metals (ETHZ) and at the Laboratoire de Métallurgie Mécanique, Ecole Polytechnique Fédérale in Lausanne (EPFL).

*Semester thesis:* The aim of the work was to avoid grain coarsening by rapidly sinter PMN-PT relaxor ferroelectrics in microwave radiation. The work was performed at the National Key State Laboratory of New Ceramics and Fine Processing, Tsinghua University Beijing, China.

*Semester thesis:* The aim of the work was to increase the strength of UHMW PE by orienting the polymer strands. This was done by drawing films on a hot stage to different ratios. The work was performed at the Institute of Polymer Technology (ETHZ).

*Industrial internship:* The aim was to improve the quality of cast abrasive wheels. This was achieved by pre-coagulating the ceramics slurries by pH change. The work was performed at the company Winterthur/Rappold in Austria in co-operation with the Institute of Nonmetallic Inorganic Materials (ETHZ).

Publications


• “Critical Current Densities of Bi-2212 Superconductor Thick Films Processed from Commercial Precursors”, D. Sager, M. Chen and L.J. Gauckler, submitted to Physica C


Presentations

• ETH Materials Colloquium (2004): “Superconductors: From Laboratory to Practice”, together with ABB Switzerland Corporate Research.

• Materials Research Society 2003 (Boston): “Enhanced Residual Secondary Phase Dissolution by Atmosphere Control in Bi-2212 Superconductors”

• American Ceramic Society 2003 (Nashville Tennessee): “Novel Precursor Reaction Pathways to Bi-2212 Superconductors”

Posters

• Euromat 2003 (Lausanne): “Novel Precursor Reaction Pathways to Bi-2212 Superconductors”


• European Superconductor Society 2001 (Copenhagen): “Grain Size Dependant Properties in Commercial Bi-2212 Powder”