ADVANCING MATERIALS PROCESSING, ELIMINATING CURRENT LIMITING MECHANISM, AND ENHANCING CRITICAL CURRENT DENSITY OF Ag-SHEATHED (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ COMPOSITE CONDUCTORS

by

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Major current-limiting mechanisms (CLMs) restrict the critical current density $J_c$ of Ag-sheathed (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ (2223) composite conductors. Overpressure (OP) processing of 2223 has been developed to enhance the connectivity and thus the $J_c$ by removing the CLMs of porosity, cracks, and Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_x$ (2212) in 2223. OP processing improved the microstructure of 2223 tapes and increased their $J_c$ by about 30%. Record $J_c$, enhanced irreversibility field, and the lowest 2212 SQUID index have been achieved in OP processed 2223 tapes. OP processing improved 2223 connectivity and resulted in higher local $J_c$ and a larger number of high $J_c$ local regions compared to conventional 1 bar processing. OP processing has been applied on the thermal slide heat treated (TSHT) 2223 tapes. It was found that adding a rolling step to the TSHT samples prior to OP processing increased the $J_c$ and irreversibility field. Quenching experiments have been carried out to gain better understanding of the role of residual liquid, which is another CLM, the formation of Pb-rich
(Bi,Pb)$_3$Sr$_2$Ca$_2$Cu$_1$O$_x$ (3221) phase in the post anneal process, and their correlations to the electromagnetic properties of 2223. $J_c$ and irreversibility field were enhanced by the PA, in which the 3221 was formed. The improvement of $J_c$ and irreversibility field was strongly correlated to the removal of residual liquid by crystallizing the liquid and forming 3221 and other phases. The 3221 was observed to begin forming in the heating step of the PA and significantly increased in the soaking step. Well-defined variations of the $J_c$, irreversibility field, and $T_c$ as a function of quenching temperature were observed during the 2223 processing. These variations were attributed to the removal/reforming of residual liquid and the changes of oxygen and Pb content in the 2223 and 2212.
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1.1 MOTIVATION

Bednorz and Muller’s discovery that superconductivity at 30 K existed in the layered cuprate LaBa$_2$CuO$_{4-x}$ opened a whole new area - high temperature superconductors (HTS) [1]. Since this discovery, oxide superconductors with high critical temperature including YBa$_2$Cu$_3$O$_x$ (92 K), (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ (110 K) and Hg$_2$Ba$_2$Ca$_2$Cu$_3$O$_x$ (130 K) have been found. Among these high temperature superconductors, Ag-sheathed (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ (2223) composite conductor is currently the primary HTS conductor available in lengths suitable for large-scale electrical applications throughout the electric power infrastructure. These include generators, transmission cables, distribution transformers, fault current limiters, motors and energy storage [2-6]. The most important criterion for assessing the conductor quality relevant to these applications is the critical current density, $J_c$. The reported 2223 self-field $J_c$ at liquid nitrogen temperature, $J_c$ (SF, 77K), is up to 70 kA/cm$^2$ for R & D short specimens [7], and up to 40 kA/cm$^2$ for long-length commercially available tape. This is, however, still smaller than the $J_c$ value industry needs to lower the cost to $25/kA-m, which is thought to be a significant price point for widespread application [8].

Current reconstruction of magneto-optic images shows that local regions in 2223 conductors have $J_c$ (SF, 77K) as high as 300 kA/cm$^2$ [9-10], and $J_c$ up to 1000 kA/cm$^2$ have been achieved in 2223 thin films [11-13]. This shows that there is much headroom in 2223 $J_c$ improvement. The studies [9-10, 14] have shown that the overall $J_c$ in 2223 conductor is mainly limited by the connectivity, which is interrupted by pores, cracks, alkaline earth cuprates (AECs), and the lower-critical temperature $T_c$ phases Bi$_2$Sr$_2$CaCu$_2$O$_x$ (2212) and
Bi$_2$Sr$_2$CuO$_x$ (2201). Even the best commercial multifilament 2223 tapes have been observed to contain up to 25% porosity [14]. These microstructural defects are inherent limitations of the conventional 1 bar thermomechanical process of 2223 conductors. Therefore, new processing methods need to be developed to improve connectivity and increase $J_c$.

The main themes of my thesis work were to develop and apply novel processing approaches to fabricate 2223 conductors and increase their $J_c$ by overcoming the problems associated with the conventional 1 bar 2223 processing, and to understand key materials science issues including current limiting mechanisms and phase transformations involved in the materials process of 2223.

1.2 OVERVIEW OF HIGH TEMPERATURE SUPERCONDUCTIVITY

One characteristic of a superconductor that it has “zero resistance”, i.e., a superconductor will lose its electrical resistance and carry current without heat loss if it is cooled to low a certain temperature, critical temperature $T_c$. The current flowing in the zero resistance superconductor is called “supercurrent”.

The other characteristic of a superconductor is that on cooling below $T_c$ it excludes external magnetic field from penetrating into its interior, which is known as the “Meissner Effect”. But the magnetic field will penetrate the sample at some high field. In fact, any applied magnetic field can enter a finite distance, the penetration depth $\lambda$, into the surface layer of a superconductor. All superconductors can be divided into two classes, Type I and Type II, based on the ratio of $\lambda$ to another fundamental superconductivity parameter, the coherence length $\xi$, which is the interaction distance between paired electrons. This ratio,
κ = λ / ξ, is called the Ginsburg-Landau parameter. If κ < 0.707, the superconductor is Type I. If κ > 0.707, the superconductor is Type II. The more fundamental characteristic distinction/definition for Type I and Type II superconductors is the sign of the interface energy between the normal and superconducting domains. Type I has a positive interface energy, and Type II has a negative interface energy. Type I superconductors do not let the magnetic flux penetrate into its interior until the magnetic field reaches a critical field $H_c$. Above $H_c$, the magnetic field penetrates the entire sample, the Type I superconductor becomes a normal state conductor. Pure element superconductors mainly belong to the Type I.

The negative normal/superconducting interface energy allows the Type II superconductor to occupy as much interfacial area as possible. When a magnetic field H is applied, the Type II superconductor is in the Meissner state and no magnetic flux from entering its interior until $H$ reaches a lower critical magnetic field $H_{c1}$. Above $H_{c1}$, the magnetic flux has penetrated into the Type II SC and the material is in a mixed normal and superconducting state between $H_{c1}$ and $H_{c2}$. With increasing field above $H_{c1}$, the superconductivity decreases until at another field $H_{c2}$. Above $H_{c2}$, the Type II superconductor becomes normal state. The penetrated magnetic flux consists of discrete quanta called fluxons. Each fluxon has a value of $2.1 \times 10^{-15}$ Wb [15] and is composed of normal state core with a radius of ξ and a vortex of supercurrent with a radius of λ.

2223 is a Type II superconductor. There is a large anisotropy of λ and ξ for 2223 between the a-b plane and c-axis direction [16]. In a Type II superconductor, the normal core cylinders are confined to small local regions, and there are still superconducting paths in the material. The transport current can pass unimpeded provided the current does not disturb the
fluxons. However, when a transport current density $J$ passes through a Type II superconductor, the fluxons feel a Lorentz force $F_L = J \times B$ that tries to push them sideways in a direction perpendicular to the directions of $J$ and $B$. The motion of the fluxons through the lattice dissipates energy and is equivalent to the resistance. Fortunately, the motion of fluxons can be stopped and pinned by normal state defects, called flux pinning centers, in the superconductor. These centers generate a force known as the flux pinning force $F_p$. When $F_L$ is equal to or greater than $F_p$, the fluxons are depinned and start to move through the material causing an energy loss, and the corresponding $J$ is defined as the critical current density $J_c$.

So whether a superconductor is in a superconducting or a normal state is not only determined by the temperature ($T$) and magnetic field ($H$), but also by the current density ($J$). As shown in Fig. 1-1, these three parameters form a three dimension at surface below which a superconductor is in the superconducting state and above which it is in normal state. From a technical application point of view, the higher these three parameters are, the better. The major task of this thesis work was to understand how to increase $J_c$.

The $J_c$ of a superconducting material is intrinsically and extrinsically limited by many mechanisms. The practical intrinsic mechanism is the flux pinning strength. The extrinsic mechanisms include porosity, deformation cracks, low $T_c$ 2212 phase, residual liquid phase, and alkaline earth cuprate (AEC) second phases. Section 1.4 of this Chapter reviews the literature about these mechanisms. The primary approaches developed in this work to pursue higher $J_c$ are to understand and reduce these current-limiting mechanisms.

In the $M$ (magnetic induction) vs $H$ (applied magnetic field) diagram of a realistic Type II superconductor, the field at which $M$ vs $H$ loop closes is known as the irreversibility field $H_{irr}$ [18-19]. For low temperature superconductors (LTS), $H_{irr}$ is very close to $H_{c2}$. For
high temperature superconductor (HTS), the motion of fluxons is more difficult to stop, i.e., they are harder to pin at the field of $H_{irr}$ below the $H_{c2}$ as the greater thermal fluctuation energy at higher temperature such as 77 K. For 2223, $H_{irr}$ is significantly lower than $H_{c2}$ due to the great anisotropy of the penetration depth $\lambda$ and coherence length $\xi$ along the $a$-$b$ plane and the $c$-axis direction [16]. There are several methods to measure the irreversibility field experimentally. In this work, the irreversibility field was characterized in two ways, one was as $H_g$, which is the field where the curvature changes sign in the extended $I$-$V$ measurement. This corresponds to the field where the vortex glass transition takes place [20-21]. The irreversibility field was also evaluated in the flux-flow regime using 1$\mu$V/cm; here we used

![Diagram](image.png)

Figure 1-1. The relationship between current density ($J$), magnetic field ($M$), and temperature ($T$) in a Type II superconductor. Below the surface, the material is the dissipation-free superconducting state. From [17]
the Kramer flux shear transition field [22], $H_k$. As a measure of the $H_{irr}$, $H_k$ is obtained by extrapolating the Kramer scaling function of the flux lattice shear, $J_c^{0.5}B^{0.25}$ plotted as a function of magnetic field, to zero.

1.3 FABRICATION OF Ag-SHEATHED (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ (2223) TAPES

2223 conductors are currently fabricated from a mixture of 2212 and other phases by the oxide-powder-in-tube (OPIT) method, as shown in Fig. 1-2. In the OPIT process, the
2223-precursor powder, which is a mixture of 2212 and oxides with a nominal composition of (Bi,Pb):Sr:Ca:Cu = 2:2:2:3, is packed into Ag or Ag alloy tube and sealed to form a billet. The billet is then drawn and rebundled to a multifilament composite and transformed into a wire shape by drawing through a series of dies with gradually decreasing diameters. Finally the wire is usually rolled into thin, flat tape. The dimensions of a typical commercial 2223 tape after the first rolling is shown in Fig. 1-2b.

The as-rolled OPIT tape/wire is then subjected to a thermomechanical cycle, shown in Figure 1-3, consisting of a first heat treatment (HT1), an intermediate rolling (IR), and a final heat treatment (FHT), shown in Fig.1-3. The FHT includes a second heat treatment (HT2) and a separate low temperature “post-anneal” (PA) seen Fig.1-3, or a heat treatment combining HT2 and PA [21, 23-25].

About 80% of the 2212 precursor powder reacts lowering the 2223 phase in HT1. It is generally accepted that the 2212 converts to the 2223 with the aid of a transient liquid, and

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Figure 1-3. Conventional 1 bar 2223 thermomechanical fabrication procedure and the mass density variation during the process. The 2223 theoretical mass density is 6.3 grams/cm$^3$. The mass density data of the 2223 tape after each fabrication step is from [14]
partial substitution of Pb for Bi was found to promote the formation of liquid and enhance the formation and stability of 2223 [26-33]. Many researchers reported that the liquid formed from the reaction between 2201 and \( \text{Ca}_2\text{PbO}_4 \), this liquid reacted with the Pb-free 2212 to form Pb-doped 2212, and then the Pb-doped 2212 reacted with AEC phases to form 2223 [27-33]. Pb has been shown to be in the 2212 lattice and cause the conversion of the crystal structure of 2212 from tetragonal for Pb-free 2212 to orthorhombic for Pb-doped 2212 [34-35]. Grivel et al. and MacManus-Driscoll et al. [36-37] reported that the formation of Pb-doped 2212 is important for forming 2223 and that Pb-doped 2212 could diminish in amplitude below 700°C in the first ramp to the 2223 formation temperature [37]. The Pb-rich phases can be formed during the heating step of the first heat treatment [37-38]. Even much work has been done studying the formation of 2223, all the details have not been elucidated because of the great complexity of the seven-component system. Another issue to which much attention has been paid is phase stability. Several groups have studied phase relations in the \( \text{Bi}_2\text{O}_3\)-SrO-CaO-CuO system over a wide temperature range [26, 39-46]. As shown in Fig. 1-4a, Majewski and coworkers investigated the phase stability and relations of the superconducting phases 2201, 2212, and 2223 [26, 39]. The stability of 2223 is also a function of the oxygen partial pressure (pO\(_2\)) and temperature. Parrell summarized and plotted related data, as shown Fig. 1-4b [37, 47-50].

Many researchers have demonstrated that IR densifies the superconducting filaments [51-56] and may improve 2223 grain alignment [57-59]. However, the IR creates an extensive network of cracks that cannot be fully healed in the subsequent heat treatments [60-63] because the 2223 formation is almost complete and there is only a little amount of liquid left which is generally believed to be required to heal the cracks. A significant amount
of porosity, ~20% as indicated by mass density measurement, remains in multifilament 2223 tape after HT2 or FHT at 1 bar [14, 64]. These residual cracks and porosity interrupt the grain connectivity and current paths, thus reducing \( J_c \). HT2 and FHT are designed to complete the 2223 formation and heal the cracks in the IR, as much as possible.

The \( J_c \) is significantly increased when a low temperature (700 ~ 800°C) post annealing (PA) is applied to the 2223 tapes after the HT2 or FHT shown in Fig.1-3. Several groups found that the PA at 750~800°C improved the \( J_c \), \( T_c \), and irreversibility field and decreased the 2212 content [23-24, 66-67]. The Pb-rich phases were observed in the PA samples. The Pb-rich phases in fully processed PA samples dissolved when the PA samples were heated back to high temperatures (~820°C) [24, 65] and the superconducting properties of the reheated samples were dramatically degraded. However, the mechanisms behind the structure-property relationship involved in the PA process are still not clear.

Many alternative methods, including hot isostatic press (HIP), room temperature and cryogenic pressing, two-axial rolling, sinter-forging, hot deformation, and melting/partial melting [68-81], have been tried as alternatives to the IR step or to have a single thermal heating step to reduce deformation cracks with the intent of improving \( J_c \). Uniaxial pressing rather than intermediate rolling has been used for short-length 2223 and it is observed that pressed tapes have better transport properties than rolled tapes [53, 55]. Although the room temperature pressing is gentler than the room temperature rolling deformation, cracks were still seen and presented along the tape direction in the pressed samples [52]. Yang et al. and Liu et al. [73, 82] have demonstrated that hot pressing can increase the \( J_c \) more than 10% compared to cold pressing. They attributed the improvement to better grain connectivity.
HIPping was developed to fabricate the Ag-sheathed 2223 tapes [68-71]. The HIPed samples have much higher density and improved $J_c$ compared to conventionally fabricated samples. However, all HIPing of 2223 prior to this thesis work was carried out in a static high-pressure system (several thousand bar). The pO$_2$ in the high-pressure Ar/O$_2$ gas decreases in the static system due to oxygen reacting with the hot metal components in the system. Furthermore, small gas leaks in the system can also decrease the total pressure of the gas mixture and pO$_2$. The instability of the reaction atmosphere in the static HIP system was
the main driving force for developing a new 2223 fabrication approach – overpressure (OP) processing - and designing a new OP system to keep the desired total pressure $P_{\text{total}}$ and $p_{O_2}$ constant throughout a run. The OP processing developed in this thesis work [25, 83-84] is a low-pressure variant of HIPping that uses a mixture of Ar and $O_2$ with a $P_{\text{total}}$ up to 200 bars to isostatically compress the conductor. The Ar applies the isostatic pressure that compresses the conductor, and the $O_2$, which can diffuse through the Ag sheath surrounding the ceramic filaments, sets the $p_{O_2}$ needed to form 2223. The isostatic pressure applied during the HT squeezes the conductor, which removes pores, heals cracks, and aligns growing 2223 grains. All of these can increase $J_c$.

### 1.4 CURRENT LIMITING MECHANISMS IN 2223 CONDUCTORS

As mentioned early, typical $J_c$ (SF, 77 K) values for the 2223 tapes range from 30 ~ 40 kA/cm$^2$ for the best commercial 2223 tape produced by the OPIT method. This is far below the local $J_c$ of 300 kA/cm$^2$ revealed by magneto-optical current reconstructure and $J_c$ values of 1000 kA/cm$^2$ achieved in 2223 thin films. [11-13]. This suggests that $J_c$ flowing in the polycrystalline 2223 bulk conductors is limited by many barriers that appear over many length scales. Since $J_c$ is defined as the critical current $I_c$ divided by the cross section area $A$, the effective current-carrying area is much smaller than the area of the whole cross section because many connectivity-limiting defects occur in 2223 tapes. These include pores, deformation cracks, and nonsuperconducting second phases.

Through-process mass density measurements carried out by Jiang et al. [14] and shown in Fig.1-3 illustrate that even though IR densifies the filaments, the mass density decreases in the final heat treatment (FHT). 2223 tape after FHT still contains about 25%
porosity and cracks. Yamada et al. [64] demonstrated that the heat treatment decreased the relative mass density of the ceramic filament from 95% to 81% for Ag alloy-sheathed tape, and from 76% to 65% for Ag-sheathed monofilament tape. They found that a relative mass density increase from 72 to 78% correlated to a $J_c$ increase from 10 to 66 kA/cm$^2$ (SF, 77K) [54]. Parrell et al. [55, 62] developed a method using the indentation hardness as a marker of mass density and porosity. They showed a very strong direct correlation between indentation hardness of 2223 tapes and $J_c$ (SF, 77 K) value.

Even though IR densifies the ceramic filaments, it breaks the 2223 grains and forms a large number of cracks, which can not be fully healed in the final heat treatment [55, 85] due to limited liquid available. Magneto-optical (MO) imaging [52, 60] showed these cracks are an important current-limiting factor. The cracks were seen as strong, bright, quasi-periodic channels in the MO images where the magnetic flux penetrated crossing whole filaments in a direction transverse to the rolling axis. By extracting and directly examining individual filaments, Cai et al. [60] found that $J_c$ was largely controlled by the unhealed cracks formed in the intermediate rolling during tape fabrication process.

It is generally accepted that 2223 forms from 2212 and alkaline earth cuprate (AEC) phases in the presence of a transient liquid phase. Residual 2212 present as half-cell intergrowths in 2223 grains and as grains in 2223 colonies was detected by multiple techniques in 2223 after HT2 or FHT [86-88]. Increases in $J_c$ were found to correlate strongly with decreases in the volume fraction of 2212 [24, 86-87]. According to the “brick wall” model proposed by Bulaevskii et al. [89], the $c$-axis transport current controls $J_c$ in 2223 tapes, namely the current jumps through larger area $c$-axis boundaries other than smaller area $ab$-axis boundaries. Microstructural and electromagnetic evidence supporting
the “brick wall” model has been found by Umezawa et al. [87, 90] in 2223 tapes with large variations in $J_c$. Umezawa et al. [87, 90] have shown residual 2212 layers located at (001) twist boundaries within 2223 grain colonies in 2223 tapes, and that the $c$-axis transport current across (001) twist boundaries controlled $J_c$.

It is well established that a transient liquid formed during the conversion of 2212 to 2223 and the partial substitution of Pb for Bi in 2223 promoted the formation of such a liquid [26-33]. The presence of the liquid was believed to decrease the melting temperature, facilitate the formation of 2223, enhance flux pinning [90-91], and help heal cracks formed during mechanical processing [52, 55, 93-94]. However, the connectivity was affected by the precipitation of 2201, Ca$_2$PbO$_4$, 3221, or residual frozen liquid from the transient liquid formed at the elevated temperature. Residual liquid was another serious current-limiting mechanism. It degrades the connectivity by coating the 2223 grains and reducing the effective current-carrying areas [91].

2201 and nonsuperconducting second phases are another current-limiting mechanism [95-98]. Horvat et al. [99] found that 2201 was located at grain boundaries and suggested reducing 2201 would lead to an increase in strong links. Dhalle et al. [100] have shown that the intragranular pinning is sample independent and high-field $J_c$ can be enhanced only by strengthening the intragranular pinning within 2223 crystals. Holesinger et al. [101-103] have shown that the nonsuperconducting phases cause cantilever type fractures of adjacent 2223 colonies during the deformation processing, and these cracks cannot be completely healed in the subsequent heat treatment. They also found that large amounts of porosity, second phases, and misaligned grain were present in the center of filaments in the 1bar processed
2223 tapes. This implied that most of the current flows in the 2223 colonies close to the Ag/2223 interface.

In summary, as shown in Fig. 1-5, even the best commercial multifilament 2223 wire \([J_c (SF, 77K) = 44 \text{ kA/cm}^2]\)] still contains up to 25% porosity. A large number of cracks formed in the intermediate rolling were not healed in HT2 or FHT. A large amount of 2212 and 2201 was left in the 2223 conductor. \(J_c\) in conventional 1atm processed 2223 conductors is locally limited by intragranular flux pinning and transport current across grain boundaries, where typically nanoscale to microscale impurities such as residual 2212, 2201, and layers of residual liquid exist and interrupt the intergrain connectivity. From the nanometer to
millimeter scale, $J_c$ is controlled by large amounts of barriers such as porosity, deformation cracks, and nonsuperconducting second phases. These extrinsic current-limiting mechanisms are intrinsic defects in the presently practiced 1 bar 2223 fabrication process. To raise $J_c$, novel processing methods and understanding of current-limiting mechanisms need to be developed. This thesis work was driven by these goals.

1.5 OVERVIEW OF THE THESIS

Ag-sheathed 2223 composite conductor is a complicated materials system. Its critical current density is constricted by many current-limiting mechanisms (CLM) associated with the conventional 1 bar thermomechanical fabrication process. This thesis work focuses on understanding and eliminating the CLMs through novel materials processing to pursue higher $J_c$. Chapter 2 describes the OP system that was designed and used in this work. In Chapter 3, the development, experimental procedure, and optimization of 2223 OP processing have been discussed. Chapter 4 presents and discusses the results of 2223 OP processing work. In Chapter 5 the 2212 reduction and the role of mechanical deformation in an experiment combining OP processing with other materials processing is presented. Chapter 6 investigates the 3221 phase formation and its correlation to the superconducting properties for 2223 composite conductors. In Chapter 7 the evolution of the phase and superconducting properties of 2223 in the process have been discussed using results from through-process quenching experiments. The general summary and conclusions drawn from this thesis work are presented in Chapter 8.
REFERENCES

5. Larbalestier et al., Power applications of superconductivity in Japan and Germany (World Technology and Engineering Center, Loyola College, MD, 1997).


CHAPTER 2. OVERPRESSURE SYSTEM

2.1 STATIC OVERPRESSURE SYSTEM

The early overpressure (OP) experiments were static OP processing which was carried out in cooperation with Bob Williams at Oak Ridge National Laboratory (ORNL). Figure 2-1 schematically shows the static OP system, which was built at ORNL. The system has no outlet. The gas mixture was made in the pressure vessel by mixing O$_2$ and Ar from separate tanks. The room temperature total pressure $P_{\text{total}}$ and oxygen partial pressure $p_{O_2}$ are set so they increase to the desired $P_{\text{total}}$ and $p_{O_2}$ at the operating temperature. It is easy to change the $P_{\text{total}}$ and $p_{O_2}$, but the gas mixture can not be replaced during OP processing. The $p_{O_2}$ decreases in the OP processing in the static system due to oxidizing the Inconel tube. Small gas leaks in the system can also decrease $P_{\text{total}}$ and $p_{O_2}$. The formation of 2223 is very sensitive to the $p_{O_2}$, so the $p_{O_2}$ variation is detrimental. The temporary solution to instable

![Figure 2-1. Schematic diagram of ORNL static OP system.](image)
pO$_2$ was to place several 2223 pellets near the samples to help maintain the desired pO$_2$. The experiment discussed in later chapters clearly shows that the pO$_2$ really matters in the last step of the process during cooling. The instability of the reaction atmosphere was the main driving force for designing and fabricating a new OP system to keep the desired $P_{\text{total}}$ and pO$_2$ constant.

2.2 FLOWING GAS OVERPRESSURE SYSTEM

A flowing gas OP system was designed and built at the Applied Superconductivity Center at UW-Madison. It is shown in Figure 2-2. The reaction chamber was made of Inconel 617 with an internal diameter of 31.8 mm and length of 1020 mm. The hot zone is

![Figure 2-2. Schematic diagram of the flow OP system. The dimensions of the Inconel 617 pressure vessel are 7.62 cm OD x 3.18 cm ID x 102 cm long.](image)
~200 mm long. The Inconel pressure vessel was externally heated by a three-zone furnace up to 900°C. High pressure, pre-mixed gas (initial gas pressure in tank is 400 bar) was used to establish the total pressure and pO₂ in the system. The maximum working pressure is 200 bar. A regulator steps down the pressure from the tank pressure to the working pressure. A set of regulators, relief valves, and meters were set up on the outlet side to maintain the reaction atmosphere inside the pressure vessel and adjust the flow rate through the system.

During OP processing, a small, controlled amount of gas flows through the whole system. Any gas consumption or loss can be replenished with this dynamic gas flow, and adjust gas flow during heating to maintain constant $P_{\text{total}}$ and pO₂ in the system. A

![Figure 2-3. Photo picture of central part of UW flowing-gas OP system, which can be operated up to 200 bar and 900°C.](image)
A thermocouple was placed into the reaction chamber close to the samples and the reaction temperature was accurately measured.

A zirconia oxygen sensor system was designed and built on the outlet side to monitor the $pO_2$ in the gas during the experiment. Much of the pressure vessel’s internal volume was filled with quartz rods minimizing the gas volume, which conserved the high-pressure gas mixture and decreased the energy stored in the system. The flowing gas OP system has advantages over the static OP system. Table 2-1 compares characteristics of the static and flowing gas OP systems.

Figure 2-3 shows the central part of the gas flowing OP system. The reaction chamber and furnace are shown at the top. The bottom part is the control panel. The valve knobs, meters, regulators, and switches were arranged in such a way that the components to control the high-pressure gas before entering the reaction chamber are built on the left side of the panel and those to control the gas flowing out of the reaction chamber are assembled on the right side of the panel.

Table 2-1. Comparison of the capabilities of the static and flow OP systems.

<table>
<thead>
<tr>
<th></th>
<th>Static System</th>
<th>Flow System</th>
</tr>
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</table>
| $P_{\text{total}}$, $pO_2$ | • Change with $T$ during run  
• Neither can be varied at a given $T$ during run | • Constant during run  
• Both can be varied at a given $T$ during run |
| $O_2$ content in system | • $O_2$ content fixed at beginning of run  
• $pO_2$ decreases if $O_2$ is consumed | • $O_2$ continuously replaced during run  
• $pO_2$ remains constant |
| Change gas mixture during a run | Cannot be changed | Can be changed |
| $H_2O$, $CO_2$, or other gases that evolve in run | Trapped in system | Can flow out of system |
2.3 SUMMARY

A flowing-gas overpressure system has been designed and built. This new dynamic high-pressure system has significant advantages over the conventional static system and it is the first of its kind used for 2223 processing. This system can be operated up to 200 bar and 900°C. In this flowing-gas system, the gas mixture is replenished and replaced by fresh high-pressure gas mixture that maintains the total pressure $P_{\text{total}}$ and oxygen partial pressure $p_{O_2}$ constant during the whole process even though some oxygen (~520 ppm) might be consumed by small leaks or metal parts at elevated temperatures. The $P_{\text{total}}$ and $p_{O_2}$ do not change with temperature variation during the heating and cooling steps and the gas mixture can be changed during the processing. These unique characteristics successfully fit the requirements of processing 2223 composite conductors under high pressure to eliminate the current limiting mechanisms including porosity and cracks, which will be discussed in the following chapters.
CHAPTER 3. OPTIMIZATION OF OVERPRESSURE PROCESSING

3.1 EXPERIMENTAL PROCEDURE

Ag-sheathed monofilament (UWB148, CX9B), 19-filament (OX70), and 55-filament (OP3734S, OX3849B) 2223 tapes were manufactured using the OPIT method at UW-Madison and American Superconductor Corp (AMSC). The tapes were typically 3mm wide and 0.16~0.21 mm thick. Samples were cut 3-cm in length. To ensure that the samples were impermeable to Ar so isostatic compression could be realized, the samples were hermetically encapsulated in a Ag foil envelope using a crimping tool (Team Company, Inc.) and a multiple-step annealing process. The sample was sealed in the Ag envelope with an O2 atmosphere.

The initial OP processing used a simple heat treatment schedule called simple heat treatment (SHT) shown in Figure 3-1a. It was consisted of only one annealing step. The temperature was varied from 804 to 824°C with an annealing time of 36 hours. This heat treatment was used in the UW-Madison flow and ORNL static OP systems with 2223 multifilament and monofilament GT samples. The flowing-gas SHT OP processing experiments were used to determine maximum temperature T_{max} for the final OP heat treatment. They were performed with \( P_{total} = 148 \) bar and \( pO_2 = 0.08 \) bar. The hermetically sealed 2223 tape samples were separated with SrZrO3 powder in an Al2O3 boat placed in the middle of Inconel tube in the OP system. The static SHT OP processing experiments were used to investigate the range of \( P_{total} \) over which OP processing can be used.
The commercial premixed 400 bar OP Ar/O₂ mixture (Matheson Gas) had a low O₂ content, 520 ppm, to set the desired pO₂ = 0.08 bar at Pₜₜₐₜ = 148 bar. It was difficult for the gas manufacturer to control precisely the O₂ content at such low values. We measured the O₂ content using a zirconia oxygen sensor and the measurement showed that the O₂ content in the tank corresponded to pO₂ between 0.075 and 0.10 bar at 148 bar. To study how the J_c was affected by changes in pO₂ over this range, final heat treatments (FHT) with a schedule shown in Figure 3-1b were performed in a normal annealing furnace on as received green tape (GT) samples after initial rolling without any heat treatment, samples after first heat treatment (HT1), and samples after intermediate rolling (IR) with Pₜₜₐₜ = 1 bar and pO₂ = 0.075, 0.09, and 0.105 bar.

From the application/industry point of view, the lower the overpressure processing pressure, the lower the cost, the easier is the protection, and the safer is the system. OP processing experiments at low total pressures (<148 bar) were carried out at ORNL to test

![Figure 3-1](image.png)

Figure 3-1. (a) Simple heat treatment (SHT) schedule for OP processing to determine T_max,  
(b) final heat treatment for 1 bar processing and OP processing.
Figure 3-2. XRD exposure surfaces prepared by (a) etching off Ag sheath and (b) polishing down to the middle layer of 2223 filaments

how low total pressure OP processing can work.

The critical current \( I_c \) was determined from self-field 77 K voltage (V)-current (I) curves using a 1 \( \mu \)V/cm criterion, and \( J_c \) is defined as \( I_c/A \) where A is the average cross section area of the 2223 filament. The mass density of the filament in monofilament 2223 was calculated from the mass, length, and cross sectional area of the superconducting filament. The cross sectional area of the superconducting filament was measured using image analysis of three transverse cross sections. The mass was measured by weighing the filament after etching off the Ag. The microstructure and composition were examined using JEOL 6100 and LEO 1530 scanning electron microscopes equipped with Noran Voyager quantitative microanalysis systems. X-ray diffraction was done at 40 kV and 25 mA in a STOE diffractometer with \( K_a \) Cu radiation. X-ray diffraction was performed on tape surfaces formed either by etching off the Ag sheath or polishing the Ag sheath and 2223 filament down to the middle layers of the ceramic filament, as shown in Figures 3-2a and 3-
3.2 RESULTS

3.2.1 $T_{\text{MAX}}$ DEPENDENCE OF MICROSTRUCTURE AND $I_C$

Figure 3-3 shows the microstructures of OP processed UW monofilament (UWB148)

![Figure 3-3](image)

Figure 3-3. Backscattered electron micrographs of UW monofilament samples OP processed using SHT (148 bar) at various $T_{\text{MAX}}$ (a) 820 °C, (b) 824 °C, (c) 828 °C, and (d) 832 °C. The dark gray grains, light gray regions, and white particles are 2223, 2212 and 2201, respectively. The black regions are alkaline earth cuprates (AEC) or CuO$_x$. 

Polishing had the capacity of revealing the phase assemblage of internal layers that were different from those of the surface seen in the etched sample due to the inhomogeneity of the 2223 reaction through the superconducting filaments.
GT samples at 148 bar for 36 hours at different $T_{\text{max}}$. The big light gray grains were unreacted 2212. Long gray grains were 2223. Black particles are alkaline earth cuprate (AEC) or CuO$_x$. The SEM images show that the sample processed at 820 °C and 824 °C using the SHT procedure had larger amount of 2223 and had more complete conversion of 2212 to 2223 compared to the samples processed at other temperatures. The conversion of 2212 to 2223 could also be evaluated based on the x-ray diffraction data using the peak intensity ratio of 2212 008 peak to the sum of 2212 008 and 2223 0010 peaks [1-2]. The XRD results show that the sample processed at 820 °C ~ 824 °C had the smallest intensity ratio and thus had the most complete 2223 formation compared to the samples treated at other temperatures.

Figure 3-4 shows the XRD patterns of UW monofilament GT samples OP processed at 824°C using SHT. These patterns were obtained by X-raying samples that were polished to

Figure 3-4. XRD patterns with peak densities normalized to the density of the 008 peak of 2223 (a) and SEM image with EDS phase analysis of internal region (b) for UW monofilament GT sample OP processed at 824°C. Phases labeled in (b) are as following: A: 3221; B: 2:1AEC; C: 2212; D: 2223; E: Ag; and F: 14:24AEC.
the center (Figure 3-2b) and with the Ag sheath etched off (Figure 3-2a). The former revealed the details of compositions and phases for the internal layers of 2223 filaments and the latter reflected those of a thin surface layer. It showed the conversion level of 2212 to 2223 was different for the internal and surface regions, which was seen from the ratio of the 008 peak intensity of 2212 to the sum of the 008 peak intensity of 2212 and 0010 peak intensity of 2223. The 2212 fraction was 11.7% and 28.3% for the surface and internal layers of 2223 filament, respectively. The inhomogeneity of 2223 formation was also observed by other researchers in the 2223 tapes even after final heat treatment [3]. In this experiment, the XRD results show that the phase assemblage was different for the internal and the surface layers of ceramic filaments. In addition to the common phases such as 2223, 2212, 2201, lead-rich phase \((\text{Bi,Pb})_3\text{Sr}_2\text{Ca}_2\text{Cu}_1\text{O}_x\) (3221), and \((\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41}\) alkaline earth cuprate (14:24 AEC) present in both the internal and surface layers, another alkaline earth cuprate \((\text{Sr,Ca})_2\text{Cu}_1\text{O}_3\) (2:1AEC) was detected in the internal layers.

Figure 3-5 displays the evolution of the microstructure in the OP processed AMSC 55-filament OP3734S GT samples using the same SHT conditions as the UW monofilament samples. This SEM image comparison qualitatively shows that the sample processed at 816°C had largest fraction of 2223 (gray grains) and the least of 2212 and 2201 (light gray or white). The quantification analysis of x-ray diffraction indicated that the samples processed at 816 °C had the most complete conversion of 2212 to 2223 evaluating by taking the intensity ratio of the 008 peak of 2212 to the sum of the 008 peak of 2212 and the 0010 peak of 2223.

Figure 3-6 shows the \(I_c\) of UW monofilament UW814B8 and AMSC 55-filament OP3734S GT samples OP processed at various \(T_{\text{max}}\) using SHT. The \(I_c\) gave maximum value
Figure 3-5. Backscattered electron micrographs of AMSC 55-filament OP3734S samples OP processed using SHT (148 bar) at various $T_{\text{max}}$ (a) 804 ºC, (b) 808 ºC, (c) 812 ºC, (d) 816 ºC, (e) 820 ºC, and (f) 824 ºC. The dark gray grains, light gray regions, and white particles are 2223, 2212 and 2201, respectively. The black big particles are alkaline earth cuprates (AEC) or CuO$_x$. The small irregular particles are pores or cracks.

Figure 3-6. $I_c$ as a function of $T_{\text{max}}$ for (a) UW monofilament UWB148 and (b) AMSC 55-filament OP3734S 2223 GT samples OP processed with SHT.
at 820°C ~ 824°C and 816°C for UWB148 and OP3734S samples, respectively, which also had the best microstructures of samples processed at lower $T_{\text{max}}$ contained more 2212 because the 2212 to 2223 conversion reaction was slower at lower temperature. Samples processed at higher $T_{\text{max}}$ contained more 2201 due to having more transient liquid in the sample at $T_{\text{max}}$ that converted to 2201 during cooling. It is apparent that the optimum OP processing temperatures for monofilament and multifilamentary tapes are different. Furthermore, when we OP processed AMSC OP3734S HT1 and IR samples with FHT (Figure 3-1b), it was found that the optimum $T_{\text{max}}$ for FHT was 822°C, which was higher than $T_{\text{max}}$ found in SHT for the GT samples. Even though the optimum $T_{\text{max}}$ for pre-heat treated tape (HT1, IR, and FHT) might be slightly different, we used $T_{\text{max}} = 822°C$ for the FHT for all samples (multifilamentary and monofilament GT, HT1, IR, and FHT).

### 3.2.2 THE EFFECT OF $pO_2$ ON $I_c$

Figure 3-7 shows the $I_c$ of GT, HT1 and IR samples processed at 1 bar with three $pO_2$ =0.075, 0.09, and 0.105 bar. For the 1 bar HT1 and IR samples, $I_c$ was essentially independent of $pO_2$ over this measuring range. For the GT samples, $I_c$ decreased with increasing $pO_2$, with the highest $I_c$ for 0.075 bar. This was consistent with reported results that the optimum $pO_2$ for 2223 formation was around 0.075 bar [4-5]. In this thesis work, the study is mainly focused on the HT1, IR, and FHT samples. The $pO_2$ is set about 0.08 bar for 1 bar and OP processing.
3.2.3 THE EFFECT OF $P_{\text{TOTAL}}$

The static OP system was used to determine how low $P_{\text{total}}$ could go and still densify the sample. GT sample with mass density greater than 90% is said to be densified. Figure 3-8 shows the mass density of monofilament GT samples as a function of $P_{\text{total}}$ after OP processing using either SHT or FHT procedure at $T_{\text{max}}$ around 824°C. It shows for $P_{\text{total}} \geq 50$ bar the density of a monofilament filament was $>90\%$, and that somewhere between 25 and 50 bar, the 2223 filament will be $< 90\%$. This suggests the OP processing can be operated at a total pressure as low as 50 bar to densify while the filaments.

Figure 3-9 indicates the variation of $I_c$ with $P_{\text{total}}$ for OP processed samples. The 1 bar and 148 bar OP processed samples were done in the UW gas-flowing OP system using the

![Graph](image)

Figure 3-7. $I_c$ of multifilamentary 2223 samples as a function of $pO_2$ with 1 bar FHT processing.
FHT cycle. The 50 and 60 bar OP processing was performed in the ORNL static OP system using a heat treatment procedure slightly different from the FHT (Figure 3-1b), which did not have the slow cooling step but had totally 96 hours of annealing time at $T_{\text{max}}$ (equal to the sum of annealing and slow cooling time for the FHT procedure in Figure 3-1b). Even though the $T_{\text{max}}$ has not been completely optimized for the ORNL 50 and 60 bar OP processing, Figure 3-9 shows the trend that the $I_c$ of both GT and IR samples increased with increasing $P_{\text{total}}$ up to 148 bar, but decreased when $P_{\text{total}}$ was raised more than 148 bar. This implies that 148 total pressure is a reasonable total pressure to achieve high critical current density. In this thesis work, the $P_{\text{total}}$ is fixed at 148 bar for OP processing.

![Relative mass density of OP processed GT monofilament tapes as a function of $P_{\text{total}}$. Density of 2223 is 6.3g/cm$^3$](image.png)
3.3 DISCUSSION

We found that $T_{\text{max}}$ for FHT was 822°C, which was slightly higher than for the OP SHT of GT samples (816°C). This higher temperature was needed because both the HT1 and IR samples had undergone HT1, in which ~80% of the 2212 in the sample was converted to 2223. At higher temperatures during HT2, more transient liquid formed in the HT1 and IR samples that may help heal cracks and enhance densification. We expect the same phenomenon occurs during OP processing. But, if $T_{\text{max}}$ is too high, too much liquid will form, which may be converted to undesirable 2212 or 2201, or residual amorphous phases during cooling. On the other hand, the results of electrical, microstructural, and compositional measurements shown in Fig. 3-3 through Fig. 3-8 suggest that optimum processing parameters, for instance $T_{\text{max}}$, depend on the tape source (manufacturer) and there

![Figure 3-9. $I_c$ of OP processed samples as a function of $P_{\text{total}}$](image-url)
exists an inhomogeneity of phase purity across ceramic superconducting filament as shown in Fig. 3-4. Different conditions may be needed to process different tapes and homogenize the filaments.

The data in Figure 3-7 for the 1 bar FHT experiments show that $I_c$ is essentially independent of $pO_2$ from 0.075 to 0.105 bar for 1 bar HT1 and IR tapes. Although we do not know the exact $pO_2$ in the OP system at 148 bar, our measurements with the zirconia oxygen sensor have bracketed it in the range 0.075 to 0.100 bar. Extrapolating from the results for the 1 bar samples, we assume $I_c$ for the OP samples would be essentially constant for any $pO_2$ between 0.075 and 0.105 bar.

The mass density measurements for static OP processed samples have demonstrated that OP processing can densify samples (relative mass density >90%) at $P_{\text{total}} = 50$ bar (Figure 3-8). An advantage of using pressures below 75 bar is that one can use an Ar/O2 mixture from a normal gas tank (~150 bar initial pressure) as the gas source for OP processing. From a cost point of view, especially for large industry production, lower pressures are desired.

Figure 3-9 shows that $I_c$ deviates the increase with pressure at $P_{\text{total}} = 195$ bar. We expected the $I_c$ would increase with pressure because higher pressure would get the ceramic filaments denser. However, the denser filaments may prevent the transient liquid from moving around to further complete the conversion of 2212 to 2223 and leave over more residual 2212, residual liquid, and second phases in the 2223 tape after OP processing. This may cause the decrease in $I_c$. On the other hand, the gas mixture we used in this 195 bar OP experiment was designed to work at $P_{\text{total}} = 148$ bar. The value of the $pO_2$ in this gas mixture may be not optimum, which may be one of the possible reasons accounting for the $I_c$
decrease at $P_{\text{total}} = 195$ bar. More OP experiments with pressures higher than 148 bar with desirable gas mixtures need to be done to verify the results shown in Figure 3-9.

### 3.4 SUMMARY

The conversion of 2212 to 2223 is a complicated process. The x-ray diffraction of polished and etched samples shows inhomogeneous distribution of composition and phases across the filament. The 2223 formation was more complete at the outer shells of filaments while more residual 2212 and 2:1 AEC phases were observed in the internal regions. The superconducting properties of 2223 tapes depend on the materials’ processing conditions. The impurities and $I_c$ in OP samples vary with the maximum anneal temperature $T_{\text{max}}$. It was found that optimum $T_{\text{max}}$ for AMSC green-tape and heat treated (HT1, IR, and FHT) samples is 816 °C and 822 °C. More residual 2212 was left due to the incomplete 2212 conversion at lower $T_{\text{max}}$, and undesired phases such as 2201 will form from remnant transient liquid formed at higher $T_{\text{max}}$ in the subsequent cooling process. Maximum $I_c$ was found in the samples processed at $T_{\text{max}} = 822 \sim 824$ °C. The 2223 filaments can be densified at $P_{\text{total}}$ as low as 50 bar. A $I_c$ apex was observed at $P_{\text{total}}$ of 148 bar for different monofilament and multifilament 2223 tapes. The total pressure used in this thesis work is, unless otherwise stated, 148 bar for the all OP processing. Although 2223 formation is sensitive to the oxygen partial pressure $pO_2$, it was found that $pO_2$ of 0.075 $\sim$ 0.10 bar was a tolerant range for AMSC 2223 tapes, within which the $I_c$ for HT1 and IR samples essentially does not change. The calculation and actual measurement show the $pO_2$ in the OP gas mixture falls in this $pO_2$ range.
REFERENCES


CHAPTER 4. OP PROCESSING SIGNIFICANTLY ENHANCED MICROSTRUCTURE AND CRITICAL CURRENT DENSITY OF 2223 TAPES

4.1 EXPERIMENTAL PROCEDURE

Most of the OP processing experiments were carried out in the UW flowing gas OP system using the schedule shown in figure 3-1b as the final heat treatment (UW FHT). The $P_{\text{total}}$ was fixed at 148 bar with $pO_2=0.08$ bar. The tape specimens came from various points in the conventional 1 bar thermomechanical process performed at American Superconductor Corp.: green tape (GT) that had not been heat treated, after the first heat treatment (HT1), after intermediate rolling (IR), and after the fully heat treated (AMSC FHT). To compare the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heat treatment and pressure conditions</th>
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<tbody>
<tr>
<td>GT</td>
<td>After first mechanical deformation and without any heat treatment</td>
</tr>
<tr>
<td>HT1</td>
<td>After first heat treatment @ 1bar</td>
</tr>
<tr>
<td>IR</td>
<td>After first heat treatment @ 1bar + Intermediate rolling (IR)</td>
</tr>
<tr>
<td>AMSC FHT</td>
<td>After first heat treatment @ 1bar + IR + second heat treatment @ 1bar</td>
</tr>
<tr>
<td>GT + 1bar</td>
<td>FHT of GT @ 1 bar</td>
</tr>
<tr>
<td>HT1 + 1bar</td>
<td>FHT of HT1 @ 1 bar</td>
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<tr>
<td>IR + 1bar</td>
<td>FHT of IR @ 1 bar</td>
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<tr>
<td>FHT + 1bar</td>
<td>FHT of AMSC FHT @ 1 bar</td>
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<tr>
<td>GT + OP</td>
<td>FHT of GT @ 148 bar</td>
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<tr>
<td>HT1 + OP</td>
<td>FHT of HT1 @ 148 bar</td>
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<tr>
<td>IR + OP</td>
<td>FHT of IR @ 148 bar</td>
</tr>
<tr>
<td>FHT + OP</td>
<td>FHT of AMSC FHT @ 148 bar</td>
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</table>
OP processing and 1bar conventional processing, the FHT heat treatment was also performed on the GT, HT1, IR, and FHT samples at 1 bar with pO₂=0.08 bar in the normal annealing furnace. The sample designations for the samples after various OP and 1bar FHT are summarized in Table 4-1.

The I-V measurements were made with a standard four-probe method in liquid nitrogen in magnetic fields up to 1 tesla. The magnetic field H was applied perpendicular to the broad tape surface (H∥c). The microstructures and chemistry were examined using SEM with EDS analysis. The 1 µV/cm criterion was used to determine the critical current I_c. The critical current density J_c was defined as I_c/A, where A is the average of two or three

Figure 4-1. Schematic diagram of atomic force microscope (AFM). From [1]
measurements of the 2223 cross-sectional area. Microstructural studies were made using a LEO 1530 SEM equipped with energy dispersive spectroscopy (EDS – Tracor Northern). X-ray diffraction was done using a STOE diffractometer with Cu Kα radiation.

The density of monocore tape was measured by mass density measurement described in Chapter 3. The porosity and topography were examined using a Digital Instruments Nanoscope IV atomic force microscope (AFM) with a silicon nitride cantilever. The 3D nature of the AFM image allows the measurement of surface features and the generation of surface statistics. The contact mode was used in the AFM examination, in which the tip was placed in mechanical contact with the sample surface at an applied force, as shown in Figure 4-1.

A new technique has been developed to determine the 2212 content in 2223 tape based on SQUID measurements [2]. In the SQUID measurement, the sample was zero field

![Figure 4-2. SQUID magnetization signals of a 2223 tape with H = 0.5 mT applied parallel to the tape axis. (a) Almost perfect shielding at the 2223 transition at ~108 K is seen in the intact tape, (b) while after rolling by 30% a large loss of magnetization and a distinct 2212 phase signal at 80 K is seen. The 2212 SQUID index is defined by the ratio AB/AO.](image-url)
cooled (ZFC) to 5 K, then at 5 K a 0.5 mT field was applied parallel to the longitudinal tape axis. The magnetic moment was measured as a function of temperature with a Quantum Design magnetometer as the temperature was increased. The SQUID measurements were made on tape before and after being rolled with a 30% reduction in thickness. Fig. 4-2 shows how the 2212 SQUID index was determined. A straight line was drawn connecting the high temperature and low temperature magnetization data for the rolled tape, then a vertical line was drawn at 80K. The 2212 SQUID index was given by the ratio of the length of the line segments AB/OA.
4.2 RESULTS

4.2.1 OP PROCESSING DENSIFIED FILAMENTS, ELIMINATED POROSITY, AND HEALD CRACKS

Figure 4-3 shows that OP processing monofilament GT + OP sample decreased the porosity compared to GT + 1bar sample subjected to an identical heat treatment of OP processing at 1 bar total pressure. The measured densities (given in the figure) confirm that OP processing increased the density. The OP processing increased the mass density from 4.91 g/cm$^3$ to 5.77 g/cm$^3$. Even though there is no intermediate rolling and the conversion of 2212 to 2223 is not completed, the GT + OP sample has reached a mass density of 5.8 g/cm$^3$ and 92% relative mass density compared to the 2223 theoretical density of 6.3 g/cm$^3$ [3]. The microstructure comparison also suggests that 2223 grains of GT+OP sample are larger and

Figure 4-4. Backscattered electron micrographs of multifilament sample after (a) HT1 + 1bar and (b) HT1 + OP. The dark gray regions, large black particles, and white particles are 2223, alkaline earth cuprates (AEC), and Pb-rich phase, respectively. The tiny irregular black regions are pores, and the light gray regions are 2212.
Figure 4-5. Backscattered electron micrographs of 55-filament OP3734S 2223 (a) IR before FHT, (b) IR+1bar and (c) IR+OP samples. The gray regions are 2223. Large black particles are alkaline earth cuprates (AEC) or CuO$_x$. Small white particles are Bi-3221 (Pb-rich phase). White line-like particles are 2212/2201. The tiny irregular and line-like black regions are pores and cracks, respectively.

better aligned compared to GT + 1bar samples.

Figure 4-4 compares the microstructure of HT1 + 1 bar and HT1 + OP samples. In HT1 + 1 bar sample, there are lots of pores and cracks in the central parts of the filaments. The 2223 grains in these regions are broken down by these pores and cracks. The edge regions of filaments are better connected compared to central regions. However, some cracks are still seen cross 2223 grains at the edges and divide them in parts, therefore the current
paths are interrupted. HT1 + OP samples are much denser. They have much fewer pores and cracks in the whole filaments and better current paths.

Figure 4-5 shows the microstructures of 55-filament OP3734S IR samples prior to FHT processing (IR), and after FHT processing at 1 bar (IR + 1 bar) and 148 bar (IR + OP). The IR and IR + 1bar samples had the following features in common: large, well-aligned 2223 grains were only observed in a thin layer near the Ag/2223 interface, and the centers of the filaments were loosely filled with poorly connected 2223 grains. These grains were separated by a large number of pores and cracks. The cracks formed by IR were not effectively healed by FHT at 1 bar, and the porosity may have even increased in the IR sample during FHT at 1bar. In contrast, the IR+OP sample appeared to have much higher density compared to IR and IR + 1bar samples and the 2223 grains appeared to be well connected throughout the filament. OP processing had significantly reduced the porosity and healed the cracks. The small white particles dispersed through the microstructure in both the IR+1bar and IR+OP samples were the 3221 phase, which had formed during slowing cooling or the post annealing step [4-6].

Figure 4-6 shows SEM images of the FHT, FHT + 1bar, and FHT + OP samples. The common feature of FHT and FHT+1bar samples was a large amount of residual porosity and cracks. In contrast, the FHT+OP sample was dense, the fabrication cracks were well healed and the porosity was effectively removed. The micrographs also show that all three samples contain current limiting phases, including discrete 2212 grains within the 2223 colonies, alkaline earth cuprates (AEC), and (Bi,Pb)$_3$Sr$_2$Ca$_2$CuO$_x$ (3221). The FHT+1bar sample (Fig. 4-6b) had the most and largest grains of 3221.
Figure 4-6 Backscattered electron SEM images for (a) FHT, (b) FHT+1b and (c) FHT+OP samples. The dominant gray regions are 2223; the large dark gray or black particles are grains of alkaline earth cuprates (AEC); the white particles are the 3221 phase; and the white streak-like grains are 2212. The irregular and line-like dark gray or black regions are porosity or cracks.
Figure 4-7. Total cross sectional area of 2223 filaments in samples processed using FHT at 1 bar and 148 bar.

That OP densifies the filament has been shown by SEM images and direct mass density measurement of monofilament tapes. The OP pressing decreased the cross section area of superconducting filaments of the multifilament tapes. Compared to the IR sample, as illustrated in Fig. 4-7, the cross section areas of HT1 + OP and IR + OP samples were reduced by 11% and 16%, respectively. Measurements of the BSCCO cross-section showed that the total cross-sectional area of the filaments was reduced from $2.99 \times 10^{-3}$ cm$^2$ for FHT and FHT+1b samples to $2.61 \times 10^{-3}$ cm$^2$ for FHT+OP samples shown in Fig. 4-6.
Figure 4-8 compares the SEM images and atomic force microscopy (AFM) topographs of longitudinal cross sections of OP and 1bar processed monocore 2223 samples. The AFM images show that the OP sample was denser (had fewer pores) and the polished surface was flatter. A small fraction of the area was porosity in the OP sample. The 1bar processed tape had much larger surface roughness compared to the OP sample. Deep
individual pores and “valleys” were present on the 1 bar sample surface, which were correlated to the loose and fractured regions in the corresponding SEM image.

### 4.2.2 OP PROCESSING SUBSTANTIALLY INCREASED CRITICAL CURRENT DENSITY AND ENHANCED IRREVERSIBILITY FIELD

#### Figure 4-9. $J_c$ of 1bar and OP processed monofilament CX9B and 55-filament OX3849B samples

The self-field (SF) $I_c$ and $J_c$ of 1 bar and OP processed 55-filament OP3734S samples listed in Table 4-2 exemplify that OP processing significantly increased $J_c$ compared to
Table 4-2. $I_c$ (SF, 77 K) and $J_c$ (SF, 77 K) of 55-filament OP3734S 1 bar and OP processed samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_c$ (SF, 77 K), A</th>
<th>$J_c$ (SF, 77 K), kA/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 bar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GT + 1bar</td>
<td>21</td>
<td>12</td>
</tr>
<tr>
<td>HT1 + 1bar</td>
<td>56</td>
<td>31</td>
</tr>
<tr>
<td>IR + 1bar</td>
<td>60</td>
<td>35</td>
</tr>
<tr>
<td>148 bar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GT + OP</td>
<td>55</td>
<td>31</td>
</tr>
<tr>
<td>HT1 + OP</td>
<td>76</td>
<td>48</td>
</tr>
<tr>
<td>IR + OP</td>
<td>88</td>
<td>59</td>
</tr>
</tbody>
</table>

identical 1 bar processing. The self-field $J_c$ (SF, 77 K) of the GT+OP sample was more than 2.5 times greater than the GT + 1bar sample; $J_c$ (SF, 77 K) of the HT1+OP sample was 55% greater than the HT1+1bar sample; and $J_c$ (SF, 77 K) of the IR+OP sample was 74% greater than the IR+1bar sample. $J_c$ (SF, 77 K) for the IR+OP sample was 58.7 kA/cm$^2$. Figure 4-9 gives the $J_c$ (SF, 77 K) comparison of 1bar and OP processed samples from different fabrication points for a monofilament CX9B and 55-filament OX3849B tapes. It shows the OP increased the $J_c$ more than 20% compared to 1bar processing, and the highest $J_c$ was found in IR samples.
Figure 4-10 shows the $J_c$ values as a function of applied field for AMSC 55-filament (OP3734S) and monofilament (CX9B) IR+OP and IR+1bar samples. In addition to the increase in self-field $J_c$, these data show that the OP processing increased $J_c$ in external fields compared to identical 1bar processing. $J_c$ (0.1 T, 77 K) of the 55-filament OP3734S IR+OP sample is 82% greater than the IR+1bar sample, having reached 22.4 kA/cm$^2$.

![Graph showing $J_c$ and log($J_c$) as a function of magnetic field at 77K for IR+OP 55-filament OP3734S and monofilament CX9B samples. The applied field was perpendicular to the broad tape surface ($H_{||c}$ axis). Self-field effects existed at low fields as shown in inset diagram [7-8]. $J_c$ at 0.1 T, 77K are marked with arrows.](image-url)
Table 4-3. $I_c$ and $J_c$ for OX3162 FHT samples subjected to 1 bar and OP processing

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_c$ (SF, 77K)</th>
<th>$J_c$ (SF, 77K)</th>
<th>$I_c$ (0.1T, 77K)</th>
<th>$J_c$ (0.1T, 77K)</th>
<th>$I_c$ (0T, 77K)</th>
<th>$J_c$ (0T, 77 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FHT + 1bar</td>
<td>168.6</td>
<td>56.4</td>
<td>70.9</td>
<td>23.7</td>
<td>208</td>
<td>70</td>
</tr>
<tr>
<td>FHT + OP</td>
<td>181.7</td>
<td>69.6</td>
<td>80.6</td>
<td>30.8</td>
<td>235</td>
<td>90</td>
</tr>
</tbody>
</table>

As shown in Table 4-3, using the $1\mu$V/cm criterion, self-field and 0.1 T $I_c$ (77 K) values of 181.7 A and 80.6 A have been achieved in AMSC’s OX3162 FHT after OP processing [9]. The corresponding $J_c$ values in self-field and 0.1 T are 69.6 kA/cm$^2$ and 30.8 kA/cm$^2$.

Figure 4-11. $J_c$ as a function of magnetic field for FHT, FHT+1b and FHT+OP samples at 77 K. The field was applied perpendicular to the broad sample surface. The inset shows $1/I_c(B)$ as a function of B for the FHT+OP sample and the linear extrapolation to 235 A for $I_c(0)$. 

kA/cm$^2$ for OX3162 FHT+OP sample. Fig. 4-11 shows that these $J_c$ values are 30% and 37% higher than the corresponding $J_c$ values of 53.4 kA/cm$^2$ and 22.5 kA/cm$^2$ for the FHT sample and 23% and 30% higher than those of 56.4 kA/cm$^2$ and 23.7 kA/cm$^2$ for the FHT+1bar sample. 30.8 kA/cm$^2$ is the highest $J_c$ (0.1 T, 77 K) value that has been reported so far for 2223 tape.

Table 4-3 compares the $I_c$ for the OX3162 FHT+1bar and FHT+OP samples. It clearly shows that OP processing increases $I_c$. The measured $I_c$ at self-field for the FHT+OP sample was 181.7 A. However, Fig. 4-11 shows the $J_c$ - $B$ curves become flattened at low

Fig. 4-12: (a) Log V as a function of Log I, (b) Log R as a function of I, and (c) Kramer plot for OP processed OP3734S IR+OP tape. The transition field of curvature sign change in the LogV-LogI or LogR-I plot was defined as the glass transition field $H_g$ and linearizing the linear region of the Kramer function to zero field as $H_K$. 
field due to very large self-field suppression effects on $J_c$ [10]. The inset shows the extrapolation of the critical current for the FHT+OP sample to zero field $I_c (0 \text{T}, 77 \text{K})$ based on the model proposed by Kim et al. [11] where $1/I_c(B) = B/I_c(0)B_0 + 1/I_c(0)$. $B_0$ is the characteristic field and $I_c(0)$ is the critical current at 0 T. The extrapolated $I_c (0 \text{T}, 77 \text{K})$ for the FHT+OP sample is 235 A, corresponding to $J_c (0 \text{T}, 77 \text{K}) = 90 \text{kA/cm}^2$. The $I_c$ and $J_c$ data for the FHT+1bar and FHT+OP samples are summarized in Table 4-3.

OP processing has been performed on another AMSC’s AP1067 FHT tape. $I_c (\text{SF, 77 K})$ 198 – 202 A and $I_c (0.1 \text{T, 77 K})$ of 90-92 A have been achieved in this FHT+OP tape.

Table 4-4. $J_c (0.1\text{T, 77K}), H_g$ and $H_k$ of 1 bar and OP processed (148 bar) samples

<table>
<thead>
<tr>
<th>Sample details</th>
<th>$J_c (\text{SF, 77K})$ kA/cm$^2$</th>
<th>$J_c (0.1\text{T, 77K})$ kA/cm$^2$</th>
<th>$H_g$ (mT)</th>
<th>$H_k$ (mT)</th>
<th>$H_g/H_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received AMSC tape</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CX9B IR, Mono-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OP3734S IR, Multi-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AP1057 FHT, Multi-</td>
<td>44.2</td>
<td>20.1</td>
<td>460</td>
<td>745</td>
<td>0.617</td>
</tr>
<tr>
<td>OX3162 FHT, Multi-</td>
<td>53.4</td>
<td>22.5</td>
<td>399</td>
<td>680</td>
<td>0.587</td>
</tr>
<tr>
<td>1 bar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CX9B, IR+1bar</td>
<td>38.7</td>
<td>13.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OP3734S, IR+1bar</td>
<td>34</td>
<td>12.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AP1057, FHT+1bar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OX3162 FHT+1bar</td>
<td>56.4</td>
<td>23.7</td>
<td>409</td>
<td>710</td>
<td>0.576</td>
</tr>
<tr>
<td>OP (148 bar)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CX9B IR+OP</td>
<td>48</td>
<td>17.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OP3734S, IR+OP</td>
<td>58.7</td>
<td>22.4</td>
<td>400</td>
<td>655</td>
<td>0.611</td>
</tr>
<tr>
<td>AP1057, FHT+OP</td>
<td>49.4</td>
<td>22.8</td>
<td>613</td>
<td>765</td>
<td>0.801</td>
</tr>
<tr>
<td>OX3162 FHT+OP</td>
<td>69.6</td>
<td>30.8</td>
<td>477</td>
<td>695</td>
<td>0.686</td>
</tr>
</tbody>
</table>
which are the highest values that have been reported. This is very important result because the self-field critical current per unit tape-width for this record $I_c$ is close to 500 A/cm-width, which is a benchmark of YBCO coated conductors.

Table 4-4 compares $H_g$ and $H_k$ for 1 bar and OP samples. The $H_g$ is in the range of 400 ~ 600 mT and $H_k$ in the range of 650 ~ 750 mT. It shows that $H_k$ exceeds $H_g$ by a

![Diagram of V-I, R-I, and Kramer plots](image)

Figure 4-13: (a) V-I, (b) R-I characteristics, and (c) Kramer plot for the FHT+OP sample with $I_c$ (SF, 77 K) over 200 A. The V-I and R-I data show $H_g$ of 613 mT and linearization of Kramer function gives $H_k$ of 765 mT.
significant margin for all the samples. The OP samples have larger $H_g$ than their corresponding 1bar processed samples, while $H_k$ does not change much for the 1bar and OP samples. This shows that OP processing increases $H_g$. The highest $H_g$ of 613 mT has been achieved in the record $I_c$ AP1057 FHT+OP sample, whose V-I characteristics and Kramer plot are shown in Fig. 4-13.

4.3 DISCUSSION

4.3.1 OP PROCESSING MORE THAN DENSIFYING FILAMENTS

The microstructure in Fig. 4-5 & 6, measurement of the cross sectional area of the core (Fig. 4-7), and measurement of filament density show that OP processing densified
the 2223 filament. If $I_c$ is constant and the filament is densified, $J_c$ increases. Thus one can ask how much of the $J_c$ increase that occurs in OP samples is due to densification and how much is caused by other factors. Figure 4-14 shows the portion of the increase in $J_c$ in

![Image](image.jpg)

Fig. 4-15. (a) SEM and (b) TEM (from T. G. Holesinger, LANL) of different forms of 2212 in 2223. Many 2212 grains in 2223 were seen in high $J_c$ OP processed 2223 sample by SEM. Discrete 2212 and 2212 intergrowth in AMSC fully heat treated 2223 tape by TEM.
HT1+OP and IR+OP samples that can be attributed to densification. For the HT1+OP sample, OP increased $J_c$ (SF, 77K) by 14.5 kA/cm$^2$ over the IR+1bar sample and densification can only account for 4.2 kA/cm$^2$ of this increase. For the IR+OP sample, OP increased $J_c$ (SF, 77K) by 25.2 kA/cm$^2$ over the IR+1bar sample and densification can only account for 6.4 kA/cm$^2$ of this increase. For this calculation, the baseline was sample IR+1bar whose $J_c$ (SF, 77K) was 33.5 kA/cm$^2$. This shows that OP increases $J_c$ by doing more than just densifying the core.

4.3.2 OP PROCESSING REDUCED LOW T$_C$ Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_x$ PHASE

The 2212 content in 2223 is believed to be a major current-limiting mechanism and has been observed in fully heat treated 2223 tapes by multiple techniques including SEM, XRD, TEM and electromagnetic measurement. [2, 12-14].

There are different types of 2212 in 2223 including discrete 2212, 2212 grains in 2223, and half-cell 2212 intergrowths in 2223. As shown in Fig.4-15a, discrete 2212 largely parallel to the axis of the tapes was seen in fully processed AMSC tape. Even in high $J_c$ OP processed 2223 tape, many c-axis aligned 2212 colonies (white streaks in Fig. 4-15b) formed as large area plates that are exceptionally well placed to obstruct any c-axis transport current were observed. These 2212 may reduce $J_c$ by obstructing c-axis current paths required to maintain long-range current continuity. Specific evidence for this in zero-field studies of bare 2223 filaments was reported some years ago [15]. Figures 4-16a & b show the psuedotetragonal and layered crystal structure of 2212 and 2223. The only difference between 2212 and 2223 is that 2223 has one more CuO-Ca double layer. It is easily understood that stacking faults can take place due to the structure similarity of 2212 and 2223.
such that half a cell of 2223 is replaced by 2212, as shown in Fig. 4-16c. This is a half-cell 2212 intergrowth. The 2212 intergrowth was observed in the TEM examination (Fig. 4-15a). 2212 intergrowths may break down the c-axis superconducting current flow and weaken flux pinning within the 2223.

Figure 4-16. Crystal structure of 2212, 2223, and 2212 intergrowth. Half unit cell with pseudotetragonal, layered structure of (a) 2212 and (b) 2223, and half of 2223 unit cell is replaced by 2212 resulting in 2212 intergrowth (c). The superconductivity takes place within the CuO layer and CaO layer serves as a spacer for CuO. The Bi(Pb)O and SrO layers serve as charge reservoirs.
Figure 4-17 is the XRD patterns for OX3162 FHT, FHT+1bar, and FHT+OP samples collected from the broad face of the tape after polishing off the Ag to expose the superconducting filaments. The exposure of central regions of filaments reveals the dominant 2223 phase as well as the secondary phases such as 2212, 3221 and AEC in the samples (Figure 4-17a). More 3221 formed in the 1bar sample compared to the FHT and OP samples.
indicated by the much stronger 3221 peak in the 1bar sample, as shown in Figure 4-17c. This was consistent with the SEM observation in Fig. 4-6. The 3221 formation will be discussed in detail in Chapters 7 and 8. As shown in Figure 4-17b, the 2212 peaks from the 2212 grains in 2223 are visible in the three samples, but the intensities of the 2212 peaks in the 1 bar and OP samples are smaller than in the FHT sample. Moreover, the full width at half maximum (FWHM) of the 0014 peaks of the 2223 phase was smaller in the OP sample than in the FHT and 1Bar samples. The broadening of 0014 reflections has been correlated with 2212 intergrowths [16-17]. These XRD results suggest the FHT processing reduced the number of 2212 grains within 2223 colonies, and OP processing reduced both 2212 grains and intergrowths within 2223 colonies resulting in smaller 2212 content relative to 1 bar processing. However, the 2212 content in 2223 revealed by XRD is much less than the 2212 white streaks shown by SEM and 2212 intergrowth shown by TEM. This may be due to resolution limitation of X-ray diffraction. Therefore, a more accurate quantitative/semi quantitative method for 2212 needs to be developed.

As illustrated at the beginning of this chapter, Cai has developed a new electromagnetic characterization technique, which defines a 2212 SQUID index, to evaluate the relative amount of 2212 in the tape [2]. As shown in Figure 4-18, IR+1bar and IR+OP OP3734S samples showed a 2212 transition kink in the magnetic moment vs temperature plot after being fractured by rolling to expose the 2212 and avoid 2212 being shielded by higher $T_c$ 2223. The calculated 2212 SQUID index was 0.50 for IR+1bar sample and 0.26 for IR+OP sample. This implies that OP remarkably reduced the 2212 content in 2223.
Figure 4-19 shows the 2212 SQUID indices for the OX3162 multifilament tape. They are 0.32, 0.29 and 0.11 for FHT, FHT+1bar, and FHT+OP samples, respectively. The much smaller value of 0.11 for the OP sample shows that OP processing decreased the 2212 content relative to the FHT and FHT+1b samples. In fact, the value of 0.11 is the smallest 2212 SQUID index that we have measured for 2223 samples from a variety of sources [2, 12, 18].

Figure 4-18. Normalized DC magnetization of IR+1bar and IR+OP 2223 tapes with 30% rolling reduction before measurement.
Figure 4-19. Magnetization moment as a function of temperature for (a) undeformed and (b) rolled FHT, FHT+1bar and FHT+OP samples obtained by SQUID magnetometer in a 0.5 mT magnetic field that was applied parallel to the long axis of the tape. The rolling reduction is 30%.

4.3.3 OP PROCESSING IMPROVED CONNECTIVITY

The removal of current obstructions of porosity, cracks, and residual 2212 should improve grain connectivity and result in better electrical connectivity for superconducting current in 2223. The magneto-optical current reconstruction (MO-CR) technique has been employed to visualize the details of current flow such as local variations in the current density, current obstruction, dissipation, and current density limiting locations in 2223.

Figure 4-20 shows MOCR images of monofilament CX9B IR+1bar and IR+OP samples [19]. Although these images indicate the nonuniform nature of current density due to the percolative nature of current flow along the tape’s polycrystalline network, the continuous red path in Fig. 4-20a shows that there is substantially better connectivity in the 148 bar OP processed than in the 1 bar processed sample by comparing the local $J_c$ values using a maximum value of 50 kA/cm$^2$ as the upper deep red value. The same data are plotted with
deep red representing 200 kA/cm$^2$ in Fig. 4-20b. Both samples show regions with $J_c > 200$ kA/cm$^2$, but there are many more of these regions and they are larger in the OP sample. In fact the peak $J_c$ in the OP sample exceeds 300 kA/cm$^2$. Higher local $J_c$ values and larger local high $J_c$ regions result in an overall larger $J_c$ value, which is consistent with transport measurement results of 39 and 48 kA/cm$^2$ for the 1 bar and 148 bar processed samples. These very high local $J_c$ values imply that there is significant $J_c$ headroom in the 2223 system.

Figure 4-20. Magneto-optical current reconstructions in 1 bar [transport $J_c$(SF, 77K) =39 kA/cm$^2$)] and OP processed [$J_c$(SF, 77K) =48 kA/cm$^2$)] AMSC monofilament samples. The local $J_c$ equal or greater than (a) 50 kA/cm$^2$ and (b) 200 kA/cm$^2$ is in dark red. The vertically aligned bar in the 1bar images is a region for which no data could be obtained due to the presence of domain structure in the imaging film [19].
4.3.4 OP PROCESSING ENHANCED IRREVERSIBILITY FIELD

Figures 4-12 a&b and 4-13 a&b show the curvature of the V-I and R-I curves changes from negative to positive with increasing magnetic field. We characterized the irreversibility field, $H_g$, as that field where the curvature changes sign, which corresponds to the field where the vortex glass transition takes place [20-21]. A surprising and significant result in Table 4-4 is the glass transition measurement [20] of the irreversibility field shows a big increase from 399 mT for the FHT sample and 409 mT for the FHT+1bar sample to 477 mT for the FHT+OP sample. A simple interpretation of OP processing is that reduction of porosity and cracking from ~ 20 % of the cross-section area in the FHT and FHT+1bar samples to less than 5 % in the FHT+OP sample enhances the active cross-section area of carrying current proportionally. In fact, measurements of the BSCCO cross-section show that the cross-section area of filaments were reduced from $2.99 \times 10^{-3}$ cm$^2$ for FHT and FHT+1bar samples to $2.61 \times 10^{-3}$ cm$^2$ for FHT+OP samples. However, Gurevich et al [22-23] has shown that dissipation in non-ohmic conductors such as superconductors is highly non-linear. Because $H_g$ is determined largely by low level dissipation-the curvature change is determined only at voltages about 100 times lower than the definition of $I_c$, the transition at $H_g$ becomes very sensitive to either sparse but strong current obstructions or many weakly dissipating barriers. Evidently OP processing reduces the severity of these barriers. The irreversibility field, evaluated in the flux-flow regime at $1\mu V/cm$, can also be characterized by the Kramer flux shear transition field [24] $H_k$, which can be obtained by extrapolating the Kramer scaling function of the flux lattice shear, $J_c^{0.5}B^{0.25}$, to zero. The Kramer plot in Fig. 4-12c and 4-13c show good linearity over a wide field range. As summarized in Table 4-4, for AMSC
OX3162 tape, \( H_g \) is 680 mT for \( H_K \) for the FHT sample, 710 mT for the FHT+1bar sample, and 695 mT for the FHT+OP sample. Significantly however OP sample appears to have more greatly enhanced the measure of low level dissipation, \( H_g \).

Table 4-4 shows the observation that \( H_K \) exceeds \( H_g \) in 2223 is universal. We find that \( H_g \) and \( H_K \) change in characteristic ways as the 2223 transformation proceeds. So far the highest values that we have attained are \( H_g = 613 \) mT for an OP processed AP1057 tape and \( H_K \) up to 740 mT for both high-\( J_c \) OP and 1 bar processed tapes. The key hypothesis that we have advanced and seek to explore is that \( H_K \) is determined by the residual 2212 content of the 2223 because flux pinning within the 2223 is weakened by those segments of the vortices that thread the residual 2212 which is seen so widely in images such as Figure 4-15. In a homogenous superconductor \( H_g \) and \( H_K \) should agree but they are clearly far apart in 2223. We hypothesize that \( H_g \) is determined principally by the population of current-obstructing defects that generate voltage at low values of current, while \( H_K \), being determined at higher voltage levels, is characteristic of more general flux flow. OP processing apparently significantly reduced the current-obstructing defects including porosity, cracks, and 2212 content in 2223, therefore enhanced irreversibility fields, especially \( H_g \).

### 4.4 SUMMARY

The OP processing has been applied on the 2223 tapes from different fabrication stages of GT, HT1, IR, and FHT as the final heat treatment. The SEM micrographs, mass density measurement, cross section measurement, and AFM images show OP processing significantly densified the 2223 ceramic filaments, removed porosity, and healed cracks. The relative mass density of GT+OP sample reached 92% even though it had not been undergone
the intermediate rolling. The OP processing reduced the cross section area by about 15%.
The OP processing effectively removed pores and deformation cracks. The SEM and AFM show OP samples had very dense, uniform, and well connected 2223 structure. There are much fewer pores and cracks in OP samples compared to 1bar samples.

OP processing 2223 tapes after GT, HT1, IR, and FHT fabrication stages results in a significant increase in $J_c$ and an enhanced irreversibility field. Record $J_c$ (0.1 T, 77 K) of 30.8 kA/cm², $I_c$ (SF, 77 K) of 181.7 A with $J_c$ (SF, 77 K) of 69.6 kA/cm², and an extrapolated $I_c$ (0 T, 77 K) of 235 A with $J_c$ (0 T, 77 K) of 90 kA/cm² have been achieved in FHT tape after OP processing. Even though $J_c$ (SF, 77 K) of 74 kA/cm² was previously reported in a 2223 tape [25], as commented in the literature [2], the external cross section dimensions (1.78 mm x ~0.08 mm) and critical current $I_c$ (~30 A) of that tape were small, so the self-field suppression of $I_c$ was also very small. So far, $J_c$ (SF, 77 K) of 69.6 kA/cm² is a record for any high current 2223 sample. In addition, $I_c$ (SF, 77 K) of 202 A has been achieved in another AMSC tape after OP processing, which is the highest value that has been reported. OP processing increased $H_g$ of a multifilament tape from 399 mT for the FHT sample and 409 mT for the FHT+1bar sample to 477 mT for the FHT+OP sample. The highest $H_g$ of 613 mT has been attained in the record $I_c$ (SF, 77 K) OP sample. The $H_k$ values of OP samples ranged from 650 to 765 mT and were higher than their corresponding $H_g$.

OP processing reduced 2212 content in 2223. The observation of smaller intensity and narrower FWHM of 2212 characteristic peaks in the XRD patterns in OP samples indicated a smaller amount of discrete 2212, 2212 colonies in 2223, and half-cell 2212 intergrowths in OP samples compared to 1 bar samples. SQUID measurements showed significant decrease in 2212 SQUID index from 0.50 for IR+1bar sample to 0.26 for IR+OP
sample, and 0.32 for FHT sample and FHT+1bar sample to 0.11 sample for FHT+OP sample. The 2212 SQUID index of 0.11 is the lowest value for the all the 2223 tapes from different sources that have been measured.

OP processing improved 2223 connectivity. Magneto-optical current reconstruction showed OP processed 2223 tapes had more uniform $J_c$ distribution, higher local $J_c$, a larger number of high $J_c$ local regions, and better connectivity than tapes that received identical 1 bar processing.

The significant increase in $J_c$ in OP 2223 samples was attributed to the OP process decreasing the density of cracks, pores, residual 2212 content, and better connectivity.

REFERENCES


18. X. Y. Cai, unpublished.


CHAPTER 5. OP PROCESSING OF THERMAL SLIDE HEAT TREATED 2223 TAPES

5.1. EXPERIMENTAL PROCEDURE

Thermal slide heat treatment (TSHT) was performed as the first heat treatment (HT1) of AMSC monofilament (CX9B) Ag-sheathed 2223 tapes by Victor Maroni at Argonne National Laboratory [1-2]. The advantage of TSHT is to control the phase balance through controlling process/conditions in HT1. In TSHT, the 2212 content is varied by changing the annealing T, t, and pO$_2$ during the heat treatment process. The microstructural and superconducting properties were studied after the intermediate rolling (IR) and OP processing were applied to the TSHT samples.

The TSHT specimen were typically 3mm wide, 0.2mm thick, and 110mm long. As shown in Figure 5-1, the TSHT procedure had 5 pO$_2$/temperature/time steps. Three variants
Table 5-1. List of $\text{pO}_2$/temperature/time set points in TSHT [1-2]

<table>
<thead>
<tr>
<th>TSHT</th>
<th>Step 1</th>
<th>Step 2</th>
<th>Step 3</th>
<th>Step 4</th>
<th>Step 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>0.08 bar $\text{pO}_2$, Get reaction going, 25% conversion</td>
<td>0.21 bar $\text{pO}_2$, break 2:1AEC, shift NSP equilibrium to 14:24 AEC</td>
<td>0.08 bar $\text{pO}_2$, keep reaction going, stop 14:24 AEC growth</td>
<td>0.04 bar $\text{pO}_2$, dissipate 14:24 AEC</td>
<td>0.08 bar $\text{pO}_2$, continues dissipation of NSPs and achieve 80% conversion</td>
</tr>
<tr>
<td>M</td>
<td>825C/300m</td>
<td>835C/300m</td>
<td>825C/1000m</td>
<td>815C/200m</td>
<td>825C/1000m</td>
</tr>
<tr>
<td>S</td>
<td>825C/300m</td>
<td>835C/300m</td>
<td>825C/200m</td>
<td>815C/210m</td>
<td>825C/200m</td>
</tr>
</tbody>
</table>

Figure 5-2. Backscattered electron micrographs of AMSC monofilament CX9B TSHT samples before OP processing (a) L, (b) S, and (c) M (see Table 5-1). The gray regions and white particles are primarily 2223 and 2212, respectively. The black particles are nonsuperconducting second phases (AEC or CuO$_x$).
of temperature and time in the THST were carried out and labeled as L, M, and S annealing time in step 3 and step 5 in which 2223 forming (L, M, and S represent “Long” (2000min), “Medium” (400min), and “Short” (300min), respectively), Table 5-1 also describes what happens in the ceramic filaments during each step.

Some of the TSHT tapes were directly subjected to OP processing using the FHT procedure, shown in Figure 5-1. These are named TSHT+OP. Intermediate rolling (IR) (~15% reduction in thickness) was performed on some of the TSHT specimens, which then underwent the OP processing, as shown in Figure 5-1. The OP processed TSHT+IR samples are called TSHT+IR+OP.

The electromagnetic characterization, microstructure, and composition analyses were carried out using standard four-probe V-I measurement, SEM/EDS, and XRD.

5.2. RESULTS

Figure 5-2 shows the microstructures of the TSHT samples. In terms of 2212 content or the completion of conversion from 2212 to 2223, Sample S was different from the other samples. The largest amount of 2212 was seen in S, in which the 2212 conversion was the least complete due to its shortest total 2212 conversion time (300min) in step 3 and step 5 compared to samples L and M. Even though L sample has a much longer conversion time of 2000 minutes than sample M 400 minutes, there is no significant difference in the amount of residual 2212 for samples L and M, which implies that 400 minute may be the minimum time needed to get the maximum 2212 conversion in the first heat treatment.
Figure 5-3. Backscattered electron micrographs of AMSC monofilament CX9B TSHT+OP samples (a) L TSHT+OP, (b) S TSHT+OP, and (c) M TSHT+OP. The gray regions and black particles are 2223 and AEC phases. The small, widely and dispersed white particles in (a) and (c) are 3221. The white streaks and white particles are primarily 2212, and light gray grains in (c) are 3221. The black particles neighboring 3221 in (c) are CuO or Cu-rich second phases (Cu atm%>70%).

Figure 5-3 shows the microstructures of the TSHT+OP samples. The TSHT+OP samples were denser compared to the TSHT samples before OP processing (Fig. 5-2). The striking feature for these three TSHT+OP samples is the size and distribution of 3221 phase. Both the size and distribution of 3221 in the sample S TSHT+OP was different from that in the other two samples, in which the 3221 phases were small and nearly uniformly dispersed.
Figure 5-4. Backscattered electron micrographs of AMSC monofilament CX9B TSHT+IR+OP samples (a) L TSHT+IR+OP, (b) S TSHT+IR+OP, and (c) M TSHT+IR+OP. The gray regions and black particles are 2223 and AEC phases. The small and dispersed white particles in (a), (b), and (c) are 3221. The white streaks and particles are primarily 2212.

The 3221 in S TSHT+OP were agglomerated and formed only a few large grains. These large 3221 grains usually were in the close proximity to CuO or Cu-rich AEC phases. The SEM images indicate that sample S TSHT+OP had more 2212 white streaks than the other two samples. The XRD data show that S TSHT+OP samples have larger 2212 peaks than samples L and M TSHT+OP.
Figure 5-4 is the SEM images for the TSHT+IR+OP samples. The microstructure of sample S TSHT+IR+OP is similar to that of samples L and M TSHT+IR+OP. No significant difference was found in the 2212 content and the grain size and distribution of 3221 in S TSHT+IR+OP samples compared to the other samples. But the S TSHT+OP samples had the largest amounts of 2212 and distinguishable 3221 morphology compared to the L and M TSHT+OP samples. Figure 5-5 displays XRD patterns for samples S, S TSHT+OP and S TSHT+IR+OP. Sample S has a large amount of unreacted 2212, which is reflected by the strong, separate 2212 peaks in the XRD pattern. OP processing converts additional 2212 to 2223 compared to S. The 2212 peak in the S TSHT+OP sample is still visible even though it

Figure 5-5. XRD patterns of S and S TSHT +OP samples. Distinct 2212 peaks are present in the patterns of S and S TSHT +OP samples. 3221 is seen in all these samples. Subscript “2” and “3” represent “2212” and “2223”. Strong 2212 and 3221 peaks are pointed out with rectangular frames.
is weak compared to sample S. However, the 2212 peaks of the S TSHT+IR+OP sample have almost disappeared.

The number of discrete 2212 and 2212 grains that are detectable by x-ray diffraction are evidently reduced by OP processing, especially in the S TSHT+IR+OP sample. Fig. 5-6 enlarges the region of the 2212 008 peak, 2223 0010 peak, and 3221 peak for S, S TSHT+OP, and S TSHT+IR+OP. As shown in Fig. 5-6a, the FWHM comparison for these three samples is S>S TSHT+OP>S TSHT+IR+OP. Furthermore, the 0010 peaks of all three samples shift to lower 2θ, which is in the direction of the 2212 008 peak. Sample S has the biggest shift. The broadening and shifting of the 2223 peaks is believed to be caused by 2212 intergrowths [4-5]. The experimental data show that S has more 2212 intergrowths compared to S TSHT+IR+OP sample, while S TSHT+OP sample has fewer 2212 intergrowths than S TSHT+IR+OP. Fig. 5-6b compares the 3221 peak for S, S TSHT+OP, and S TSHT+IR+OP.

Figure 5-6. (a) XRD pattern of 2212 008 peak and 2223 0010 peak and (b) 3221 peak for S and S TSHT+OP, and S TSHT+IR+OP samples. All the intensities were normalized to the 008 peak of 2223. The calculated 2θ position (dash lines) of the 2212 008 peak and the 2223 0010 peak are from [3-5].
Figure 5-7. $J_c$ as a function of TSHT processes for monofilament CX9B tapes.

Figure 5-8. (a) Log V-Log I, (b) Log R- Log I, and (c) Kramer function of S TSHT+OP sample
samples. It shows sample S has more 3221 than the other two, which have similar amounts of 3221.

The $J_c$ of monofilament TSHT+OP samples is plotted in Figure 5-7. The L TSHT+OP and M TSHT+OP have higher $J_c$ than S TSHT+OP, which corresponds to its undesirable microstructure, i.e., more unconverted 2212. The $J_c$ values of TSHT+IR+OP samples are also given in Fig. 5-7. The $J_c$ data of the TSHT+IR+OP samples show a very interesting trend,

Figure. 5-9. (a) Log V-Log I, (b) Log R- Log I, and (c) Kramer function of S TSHT+IR+OP sample
which is that the S TSHT+IR+OP sample had the highest \(J_c\) value among the TSHT+IR+OP samples. We have already seen that the S TSHT+OP sample had the lowest \(J_c\) value. From the material processing point of view, the only difference between S TSHT+IR+OP and S TSHT+OP is that the former has an additional intermediate rolling (IR) step before undergoing OP processing. This implies that the IR played an important part in increasing the \(J_c\).

Figures 5-8 and 5-9 show the results of extended V-I curves and Kramer plots for S TSHT+OP and S TSHT+IR+OP samples. S TSHT+OP and S TSHT+IR+OP samples attained \(H_g\) of 341 mT and 419 mT, which is defined by the field at which curvature in the LogV-Log I and LogR-I curves changes sign. This is a large increase in \(H_g\). The \(H_k\) extrapolated from the linear region of the Kramer plot to zero field is 600 mT and 640 mT for the S TSHT+OP and S TSHT+IR+OP samples. The \(H_k\) is slightly higher for the S TSHT+IR+OP sample compared to the S TSHT+OP sample. The \(H_g\) and \(H_k\) values for other
samples are summarized in Table 5-2. These data show that adding IR prior to OP processing increased both the $H_g$ and $H_k$ for all the TSHT samples.

5.3 DISCUSSION

Compared to samples M and L, the sample S had the shortest total anneal time at step 3 plus step 5 to convert 2212 to 2223 (Table 5-1). More 2212 was expected to be in the sample S compared to samples L and M. So it was not surprising that the largest amount of unreacted 2212 was seen in the SEM image of the sample S in Fig. 5-2b. The conversion of

![XRD patterns of samples S TSHT+OP, M TSHT+OP, and S TSHT+IR+OP. All peak intensities are normalized to the intensity of 2212 008 peak. The 2212 peaks are pointed out by dotted rectangular frames. Distinct 2212 peaks are present in the pattern of sample S TSHT+OP.](image-url)
2212 to 2223 was more complete in some regions, for instance in the right top part of Fig. 5-2b; and it was far from complete in other regions such as in the left bottom region of Fig. 5-2b. The very strong 2212 peaks observed in the XRD pattern of the sample S (Fig. 5-5), confirmed that a large number of 2212 grains had not reacted to form 2223 in the sample S. Figure 5-6a shows that sample S had more 2212 intergrowths in the 2223 than samples M and L.

For the TSHT+OP samples, Fig. 5-7 demonstrates that the sample S TSHT+OP has a lower \(J_c\) than samples M TSHT+OP and L TSHT+OP; the latter two have similar \(J_c\). From a microstructural point of view, the most important microstructure characteristics that distinguish S TSHT+OP from M TSHT+OP and L TSHT+OP were the distribution the 3221 and 2212 content. As shown in Fig.5-3, sample S TSHT+OP had fewer but larger 3221 grains compared to a much larger number of tiny 3221 particles dispersed in L TSHT+OP and M TSHT+OP. As shown in Fig. 5-10, 2212 peaks at about 23.2° and 35°(2θ) were clearly seen in the XRD pattern of sample S TSHT+OP, but only a very small 2212 peak at 35° was seen in the XRD pattern of M TSHT+OP. Its 2212 peak at 23.2 was so weak that it could not be separated from the 2223 0010 peak. This indicated that sample S TSHT+OP has a larger amount of 2212 than sample M TSHT+OP. The situation was totally changed when an IR process was performed on the TSHT samples and then OP processing was applied on the TSHT+IR sample. As shown in Fig.5-7, the S TSHT+IR+OP sample had the highest of the \(J_c\) samples. The \(J_c\) trend of the TSHT+IR+OP samples was in the opposite direction compared to the TSHT+OP samples. The SEM micrographs (Fig.5-4) showed that the microstructure of all three TSHT+IR+OP samples was similar. It was hard to identify them
Figure 5-11. Backscattered electron micrographs of monofilament CX9B 2223 tapes (a) HT1, and immediately after (b) CIP (4000 bar) and (c) IR. The gray regions are 2223. Large black particles are alkaline earth cuprates (AEC) or CuO. White particles are Bi-2212. The small irregular and line-like black regions are pores and cracks.
based on their SEM micrographs, whereas the S TSHT+OP sample had a 3221 distribution that was different from samples L TSHT+OP and M TSHT+OP. From a processing point of view, the only difference between TSHT+OP and TSHT+IR+OP sample was the latter had an additional IR process. The $J_c$, SEM, and XRD results suggested that IR enhanced $J_c$ and increased the irreversibility fields $H_g$ and $H_k$, and changed the microstructure.

Why did the IR deformation improve the superconducting properties of 2223? To answer this question, SEM has been conducted to exam the microstructures of monofilament CX9B and multifilament OX3162 HT1 samples without any additional mechanical deformation, and HT1 samples immediately after cold isostatically pressing (CIP) (4000 bar), and HT1 samples immediately after intermediate rolling (IR) (~15% reduction in thickness). Figures 5-11 and Figure 5-12 show that intermediate rolling increased the density of the samples. This is not a new result and has been reported before [6-9]. In fact, Holesinger et al. [10-11] have shown that IR breaks 2212 grains. The mechanical deformation broke grains and densified the ceramic core for both monocore and multifilamentary tapes. The grain sizes (for instance AEC) were smaller in the CIP and IR samples compared to the HT1 sample before deformation. As expected, the IR, which was shear deformation, caused more serious deformation than CIP, which was an isostatic deformation. Figure 5-13 shows that IR fractured and exposed internal, unreacted 2212 in 2223 grains, and formed a large number of deformation cracks. These exposed residual 2212 grains could form transient liquid, that got access to AEC phases by forming along the cracks formed by the mechanical deformation. The transient liquid reacted with AEC phases to form 2223, i.e., $\text{transient liquid + AEC second phases} \rightarrow 2223$, where 2212 was partially melted and formed liquid [12-14]. The
Figure 5-12. Backscattered electron micrographs of 55-filament OX3849B 2223 tapes (a) HT1, and immediately after (b) CIP (4000 bar) and (c) IR (15% thickness reduction). The gray regions are 2223. Large black particles are AEC or CuO. The small irregular and line-like black regions are pores and cracks.
2212 conversion can occur at many various locations between the fragmented 2212 and second phase grain after deformation.

The cracks acting as “channels” filled with liquid that allowed rapid liquid phase cation diffusion. As a result, with mechanical deformation, the 2212 conversion was more

Figure 5-13. Backscattered electron micrographs of OX3849B 2223 tapes (a) HT1, (b) IR sample, and (c) IR sample plus additional 7 % IR and OP processing, and (d) monofilament CX9B IR tape. The gray regions are 2223. Large black particles are alkaline earth cuprates (AEC) or CuO. White particles are 2212. The irregular and line-like black regions are pores and cracks.
complete and less residual 2212 was left. As shown in Fig. 5-10, the 2212 peaks almost
disappeared in the XRD pattern of S TSHT+IR+OP sample, but they were well-defined in
the XRD of sample S TSHT+OP. This confirmed that IR reduced 2212 content. The 2212
reduction by IR may account for the $H_k$ increase from the TSHT+OP sample to
TSHT+IR+OP samples because $H_k$ is possibly determined by the 2212 within the 2223 and
flux pinning within the 2223 is weakened by those segments of the vortices that thread the
residual 2212 intergrowth.

In Chapters 6 and 7, studies that show the Pb-rich phase 3221 comes from residual
liquid, which may form from 2212 at elevated temperature. In sample S TSHT+OP (without
IR), the transient liquid formed during OP processing might be isolated in some regions
where originally there were many unreacted 2212 grains seen in Fig. 5-2b. The liquid might
not move around freely because there were few cracks available for delivering the transient
liquid to form 2223. This residual liquid could finally convert to some big 3221 particles in

\[ J_c \]

\[ \text{IR reduction (1/Thickness)} \]

Figure 5-14. Schematic plot of $J_c$ as a function of intermediate rolling (IR) reduction or
1/thickness for 1atm and OP processing.
certain regions as shown in Fig. 5-3b. In contrast, the TSHT+IR+OP sample had a network of deformation cracks, which helped transport the transient liquid in a large scale throughout the sample to form 2223.

Vase et al. [15] and Grasso et al. [16-17] have demonstrated that $J_c$ or $J_e$ ($J_e$: engineering critical current density, defined as $I_e/A_{tape}$) depended on filament thickness. There was a maximum in the thickness dependence of $J_c$, which is schematically shown in Figure 5-14. They attributed the decrease in $J_c$ seen at small thickness to the formation of cracks and at large thickness to poor texture. So there was optimum tape thickness at intermediate rolling reduction for standard 1 bar processing. The cracks formed in IR cannot be fully healed and the filament density even appeared to decrease in the final 1 bar processing [6]. OP processing healed cracks and densified the superconducting cores. So smaller thickness or larger IR reduction of 2223 tapes that may provide more grinding and mixing may be possible using OP processing. With larger IR reduction for 2223 tapes, it may be possible to further reduce the 2212 content, and $J_c$ may be further increased by healing cracks using OP processing. However, the 2223 processing is complicated. The changes made in the IR may require reoptimizing on other processing parameters such as the annealing temperature and time in the final heat treatment. Many additional detailed studies may be needed to get a better understanding of the grinding and mixing process and the general processing-microstructure-property relationship for 2223 composite conductors.

5.4. SUMMARY

OP processing has been applied to thermal slide heat treated (TSHT) 2223 tapes. It was found that the 2212 content after TSHT and intermediate rolling (IR) had significant
effects on the properties of OP processed TSHT tapes. Without IR, the TSHT sample with more 2212 had lowest $J_c$ after OP processing. A smaller number of 3221 precipitates with larger sizes was also observed in the sample with more 2212 after OP processing whereas small, well dispersed 3221 precipitates were seen in those samples with less 2212. XRD confirmed that the 2212 content in the TSHT sample without IR was reduced by OP processing, but the sample with more 2212 after TSHT still had a larger amount of 2212 after OP processing.

Adding IR to the TSHT samples prior to OP processing increased $J_c$, $H_g$, and $H_k$. $J_c$ (SF, 77 K) and $J_c$ (0.1 T, 77 K) of the TSHT sample with IR and more 2212 were increased 50% and 69%, respectively, after OP processing compared to the same OP processed tape without IR. $J_c$ (SF, 77 K) and $J_c$ (0.1 T, 77 K) of the TSHT sample with IR and less 2212 after TSHT were increased more than 16% and 30%, respectively, after OP processing compared to the corresponding OP processed non-IR tapes. OP processed TSHT samples with IR had more than 17% increase in $H_g$ and 7% increase in $H_k$ compared to the OP processed TSHT samples without IR. The XRD showed that IR followed by OP reduced the 2212 content. The 2212 content in the TSHT samples did not affect the size and distribution of 3221 if the IR had been applied to the samples prior to OP processing. SEM examinations of samples with different mechanical deformations showed that IR densified the filaments, exposed the 2212 that was covered with 2223, and formed a large number of cracks. This exposed 2212 may form transient liquid that reacts with AEC phases to form additional the 2223 reducing the residual 2212. The cracks formed in IR may serve as mass-transport channels delivering transient liquid throughout the sample to allow the AEC phases and liquid to react to form 2223.
REFERENCES


CHAPTER 6. PHASE FORMATIONS AND ELECTROMAGNETIC PROPERTIES OF POST ANNEALED 2223 TAPES

The low temperature anneal post anneal (PA) significantly enhances the $J_c$, $H_g$, and $H_k$ of 2223 tapes [1-4]. The $J_c$ 2223 degraded and 3221 phase dissolved when post annealed samples were heated back and annealed at a high temperature of 822°C [4]. However, the mechanisms behind these phenomena have not been understood yet. The great complexity of 2223 materials system is one of the biggest obstacles to understanding the PA process. OP processing has been important because it has eliminated two major operative current-limiting mechanisms, cracks and pores, allowing us to explore the post anneal process with fewer uncontrolled variable. The first part of this Chapter concentrates on investigating the effects of the PA on the samples subjected to OP processing of three consecutive processes (see Fig.6-1a) of HT2, low temperature post HT2 anneal (PA1), and a higher temperature post anneal (PA2).

The characteristic microstructure feature associated with the enhanced electromagnetic properties is that Pb-rich phase (Bi,Pb)$_3$Sr$_2$Ca$_2$Cu$_1$O$_x$ (3221) formed in the PA samples. Therefore, to understand the origin of 3221 and the intrinsic relationship between the 3221 formation and the enhancement of superconducting properties in the PA samples is very important to control the materials processing of 2223 composite conductors to improve their performance. The 3221 was observed to form in less than 3 hours. Fast reaction is a typical behavior of liquid assisted reaction. This hints that 3221 may come from liquid. The second part of this Chapter focuses on proving that 3221 comes from liquid.
Quenching and slow cooling have been employed to artificially change the amount of residual liquid in the samples, then a short time PA has been carried out on the quenched and slow cooled samples to explore the origin of 3221 and its effects on the superconducting properties of 2223.

6.1 EXPERIMENTAL PROCEDURE

As shown in Figure 6-1a, HT2 and two post HT2 annealing labeled PA1 and PA2

![Diagram](image)

Figure 6-1. (a) Schematic diagrams for OP heat treatments of HT2, PA1, and PA2 and (b) the heat treatment schedule for the quenching and slow cooling HT1 and 3-hour PA.
were performed at $P_{\text{total}} = 148$ bar and $pO_2 = 0.08$ bar. The temperature/time points for HT2, PA1, and PA2 are 822°C/72 h, 783°C/24 h, and 817°C/48 h, respectively. A slow cooling step of 1°C/h for 24 h was incorporated in the HT2. The ramping rates were 4°C/min for heating and 1.5°C/min for cooling. The HT2, PA1, and PA2 were performed on AMSC monofilament CX9B tape that had received an intermediate rolling. Samples taken out at the end of each process were labeled OP-HT2, OP-PA1, and OP-PA2.

For the quenching and slow cooling experiments to explore the origin of 3221 and its effects on the superconducting properties of 2223, 5cm-long samples were cut from monofilament CX9B and multifilament OX3849B GT tapes produced by American Superconductor Corp. (AMSC). The reason GT tapes rather than HT1, IR, or FHT tapes were used in this work was because the 2212 had not been converted to 2223 in the GT tapes, and more liquid in the GT tape compared to the tapes from other fabrication stages will form at elevated temperature so that more residual liquid can be retained in the quenched samples. As shown in Figure 6-1b, the samples first were annealed at 822°C for 36 hours, then they were either slow cooled to room temperature or quenched to room temperature by being quickly taken out of the furnace and put on an Al metal block. The quenched and slow cooled samples were identified as Q and SC samples, respectively. In the slow cooling, the sample was cooled at a rate of 1°C/hour from 822°C to 774°C and 1.5°C/min from 774°C to room temperature. The quenched and slow cooled samples subsequently underwent a short time post annealing (PA) at 783°C for 3 hours. The corresponding PA samples were labeled as Q+PA and SC+PA. The whole heat treatment is shown in Fig. 6-1b. The heat treatment was
performed in a gas mixture of N₂ and O₂ with 1 bar total pressure and 0.08 bar oxygen partial pressure.

The V-I characteristics of 2223 samples were measured using the standard four-probe technique in liquid nitrogen in magnetic fields up to 1 T applied approximately parallel to the c axis. The criterion for $I_c$ is $1 \mu V/cm$ and $J_c$ was defined as $I_c/A$, where A is the average area filament cross sections. Microstructural examinations were made using JSM-6100 and LEO 1530 scanning electron microscopes. Composition analysis was conducted using energy dispersive spectrometry (EDS) with the LEO 1530 SEM. X-ray diffraction was performed on polished samples using a STOE diffractometer with Cu Kα radiation. The magnetic moment as a function of temperature was measured using a Quantum Design magnetometer in a field of 0.5 mT applied along the longitudinal direction of the sample. The samples were reduced 30% in thickness by rolling before SQUID measurement, and the crushed sample was zero-field cooled (ZFC) to 5 K in the SQUID measurements. The samples were prepared for magneto-optical (MO) imaging by chemically removing the Ag sheath from the broad face of the tape using a NH₄OH/H₂O₂ etch. MO imaging was performed by placing a ~2 mm thick ferromagnetic Bi-doped Y-iron-garnet film directly on the exposed ceramic filament of the broad tape surface. Samples were zero field cooled to 11 K, and then they were imaged in a magnetic field of 1200 Oe applied perpendicular to the broad surface of the tape.

6.2 RESULTS

6.2.1 OP POST ANNEAL PROCESSING OF 2223 TAPES

Table 6-1 shows the results of the electromagnetic measurements. The first low temperature anneal, PA1, increased the $J_c$ (SF, 77K) from 34.6 kA/cm² to 41.3 kA/cm² and $J_c$
Table 6-1. $J_c$, $H_g$, and $H_k$ of OP-HT2, OP-PA1, and OP-PA2 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_c$ (SF, 77K) kA/cm$^2$</th>
<th>$J_c$ (0T, 77K) kA/cm$^2$</th>
<th>$H_g$, mT</th>
<th>$H_k$, mT</th>
<th>$H_g$/$H_k$</th>
<th>2212 SQUID index</th>
</tr>
</thead>
<tbody>
<tr>
<td>OP-HT2</td>
<td>34.6</td>
<td>13.7</td>
<td>500</td>
<td>580</td>
<td>0.86</td>
<td>0.32</td>
</tr>
<tr>
<td>OP–PA1</td>
<td>41.3</td>
<td>16.8</td>
<td>550</td>
<td>700</td>
<td>0.79</td>
<td>0.23</td>
</tr>
<tr>
<td>OP-PA2</td>
<td>25.8</td>
<td>8.4</td>
<td>370</td>
<td>480</td>
<td>0.77</td>
<td>0.35</td>
</tr>
</tbody>
</table>

(0.1T, 77K) from 13.7 kA/cm$^2$ to 16.8 kA/cm$^2$. PA1 also significantly enhanced the irreversibility fields $H_g$ and $H_k$. $H_g$ was improved from 500 mT to 550 mT and $H_k$ from 580 mT.

Figure 6-2. SEM image (a) and EDS maps of elements Pb (b), Cu (c), and Ca (d) for OP-HT2 sample. The gray regions are 2223. Black particles are mainly 2:1 alkaline earth cuprate (AEC) phases. White streaks are 2212. No Pb-rich phase 3221 was found.
mT to 700 mT. However, $J_c$ and irreversibility fields dramatically dropped after the second post anneal PA2. The $J_c$ (SF, 77K) and $J_c$ (0.1T, 77K) of OP-PA2 samples decreased about 40% and 50% to 25.8 kA/cm$^2$ and 8.4 kA/cm$^2$ compared to OP-PA1 samples, respectively. There are also about 30% decreases in $H_g$ and $H_k$ from OP-PA1 to OP-PA2 samples.

Figure 6-2a shows the microstructure of OP-HT2 samples. Even though the major phase is gray 2223, white 2212 streaks are still seen in the OP-HT2 sample. The SQUID measurement indicates the 2212 SQUID index is 0.32 for OP-HT2 sample (Table 6-1). EDS mapping identifies the majority second phase is 2:1 AEC, which is shown as bright particles.

Figure 6-3 SEM image (a) and EDS maps of elements Pb (b), Cu (c), and Ca (d) for OP-PA1 sample. The gray regions are 2223. Black particles are mainly 14:24 AEC phases. White streaks are 2212. White particles are Pb-rich phase.
in Fig. 6-2d. A small amount of 1:1 AEC phase was observed in OP-HT2 samples. There were no significant Cu-rich 14:24 AEC phases seen in the EDS Cu map (Fig. 6-2c) of the OP-HT2 sample. Furthermore, no white Pb-rich 3221 phase was observed in the SEM image (Fig.6-2a) and no 3221 regions were seen in the Pb map (Fig.6-2b).

Figure 6-3 shows the microstructure and corresponding EDS maps of OP-PA1 samples. There are two striking microstructural features for OP-PA1 samples. One is a large amount of 3221 phase formed in the OP-PA1, which are seen as widely dispersed white phases in the SEM image (Fig.6-3a). Bright Pb-rich regions were clearly seen in the Pb-
element map corresponding to these 3221 particles. The other is a significant amount of 14:24 AEC phase formed in the OP-PA1 samples. Black particles in the SEM image were identified as 14:24 AEC, which were seen in the Cu map either as bright individual big regions or small, bright spots. The Ca map also shows some 2:1 AEC and 1:1 AEC phases left in the OP-PA1 sample.

Figure 6-4 shows the SEM and EDS maps for the OP-PA2 sample, which was obtained by heating the OP-PA1 sample to an anneal temperature higher than that of PA1 for 48 hours. The consequent result for the higher temperature anneal was that phase assemblage was changed back to that similar to OP-HT2. As seen in Fig. 6-4a and 6-4b, 3221 dissolved and was no longer seen in the SEM image and Pb map. There was no Cu-rich 14:24 AEC bright regions seen in the Cu map (Fig. 6-4c) and big 2:1 AEC particles were observed in the Ca-map (Fig. 6-4d).

6.2.2 PHASE FORMATIONS AND ELECTROMAGNETIC PROPERTIES OF QUENCHED AND SLOW COOLED 2223 TAPES

Figures 6-5a and 6-5b show the SEM images of monofilament CX9B Q and SC samples. The majority phase for the both two samples was the gray Bi-2223 phase. Unreacted 2212 and AEC phases were also observed in samples Q and SC. A small amount of tiny 3221 grains was observed in sample Q, but not seen in slow cooled samples. The x-ray diffraction (XRD) results confirm the phase assemblage of the quenched and slow cooled samples revealed by SEM images. As seen in Fig.6-5c, weak characteristic (300/111) peak from the 3221 phases were seen in the XRD pattern of the quenched samples, but no 3221 was seen in the slow cooled samples. About 71% and 83% 2212 had been converted to 2223
in the quenched and slow cooled samples respectively, based on the XRD data evaluated by taking the intensity ratio of the 2212 008 peak to the sum of the 2212 008 peak and the 2223 0010 peak. Figure 6-6 shows the SEM images and XRD patterns for the quenched and slow

Figure 6-5. The SEM images of the monofilament CX9B (a) quenched Q and (b) slow cooled SC samples, and (c) the XRD patterns of the Q and SC samples.
cooled multifilament OX3849B samples. Both SEM and XRD show the prominent phase was 2223. There was no 3221 phase in the quenched and slow cooled samples. The XRD

Figure 6-6. The SEM images of multifilament OX3849B (a) quenched Q and (b) slow cooled SC sample, and (c) the XRD patterns of the Q and SC samples.
Figure 6-7. The SEM images of the monofilament CX9B (a) Q+PA and (b) SC+PA samples, and (c) the XRD patterns of the Q+PA and SC+PA samples. Tiny white particles in (a) and (b) are 3221.

shows 80% 2212 in the sample Q and 88% 2212 in the sample SC had been converted to 2223.

Figure 6-7 displays the SEM micrographs and XRD patterns for the Q+PA and SC+PA monofilament CX9B samples. The most striking feature of the Q+PA and SC+PA CX9B samples is the Pb-rich 3221 phase has appeared in these samples after the PA. As shown in Fig. 4a and 4b, there is more 3221 in the Q+PA sample compared to the SC+PA sample. The XRD result further shows that there is 82% more 3221 in the Q+PA sample
than in the SC+PA sample. The XRD data also show that the 2223 slightly increased in the post annealed samples. The 2212 conversion was 77% and 85% for the CX9B Q+PA and SC+PA samples, respectively.

Figure 6-8. The SEM images of multifilament OX3849B (a) Q+PA and (b) SC+PA samples, and (c) the XRD patterns of the Q+PA and SC+PA samples. Tiny white particles in (a) and (b) are 3221.
Figure 6-9. The $I_c$ of the (a) monofilament CX9B and (b) multifilament OX3849B tapes. The heat treatment conditions for sample Q-84h was shown in Fig.6-14a.

Figure 6-8 shows SEM images and XRD results for the multifilament OX3849B Q+PA and SC+PA samples. The 3221 was clearly seen in the quenched and slow cooled samples after post anneal. The XRD shows that the amount of 3221 in the Q+PA sample is
43% more than that in the SC+PA sample. 84% of the 2212 in the Q+PA sample and 87% in the SC+PA samples had been converted to 2223.

Figure 6-9 shows the critical current $I_c$ for the quenched and slow cooled CX9B and OX3849B samples before and after post annealing. For the monofilament CX9B tape (Fig.6-9a), the quenched sample has much smaller $I_c$ of 6.5 A than that of 20 A for the slow cooled sample. After the 3-hour post annealing, substantially larger $I_c$ occurred in the quenched samples compared to the slow cooled samples. PA almost tripled the $I_c$ of the Q sample to 17 A for the Q+PA sample, but increased the $I_c$ of the SC sample only by 20% to 24 A for the

Figure 6-10. The Log V-Log I curves as a function of applied magnetic fields for the monofilament CX9B (a) Q, (b) Q+PA, (c) SC, and (d) SC+PA samples.
SC+PA sample. For the multifilament tape, shown in Fig. 6-9b, the $I_c$ of the quenched sample, 13 A, was about a half of that of the slow cooled samples, 24.5 A. PA increased the $I_c$ of the quenched sample by 85% to 24 A for the Q+PA sample and increased the $I_c$ of the slow cooled sample by 14% to 28.5 A for the SC+PA sample.

Figure 6-10 is the extended V-I curves for the quenched and slow cooled CX9B samples before and after post annealing. The curvature of the V-I plots change from negative to positive with increasing magnetic field. We characterized the irreversibility field, $H_g$, as that field where the curvature changes sign, which corresponds to the field where the vortex glass transition takes place [1, 5]. A surprising and significant result in Fig. 6-10 is the glass transition measurement [5] of the irreversibility $H_g$ field shows a huge increase from 48.2 mT
for the Q sample before PA to 203.9 mT for the Q+PA sample. However, there is essentially no change in $H_g$ for the slow cooled sample before and after post annealing. The $H_g$ is 243 mT for the SC sample and 242.6 mT for the SC+PA sample.

The irreversibility field, evaluated in the flux-flow regime measured at 1$\mu$V/cm, can also be characterized by the Kramer flux shear transition field [6] $H_k$, which can be obtained by extrapolating the Kramer scaling function of the flux lattice shear, $I_c^{0.5}H^{0.25}$, to zero. The Kramer plot in Fig. 6-11 gives $H_k$ of 190 mT for the Q CX9B sample, 575 mT for the Q+PA sample, 614 mT for the SC CX9B sample, and 665 mT for the SC+PA CX9B sample. The quenched sample appears to have a dramatic increase in $H_k$ after post annealing while its counterpart, slow cooled sample, has a slight increase in $H_k$.

6.3. DISCUSSION

The $J_c$ and irreversibility field $H_g$ and $H_k$ significantly increased in the OP-PA1 process and decreased in the OP-PA2. The 3221 was not observed in OP-HT2 and major alkaline earth cuprate phase was found to be 2:1 in the OP-HT2 sample. The microstructure characteristics associated with the $J_c$, $H_g$, and $H_k$ changes were that 3221 was presented after OP-PA1 and disappeared after OP-PA2. The 3221 precipitation was accompanied by the formation of 14:24AEC. 3221 precipitated in the OP-PA1 process and the major AEC phase changed to 14:24. The 3221 dissolved in the subsequent OP-PA2 heat treatment and the majority of second phases were changed back to 2:1. The formation of 3221 was locally observed to have formed in close proximity to particles 14:24 AEC as seen by points A, C, and D in Fig. 6-12. However, no 3221 was found in the region surrounding 2:1 AEC particle
B. The SEM image and EDS maps clearly show the collocation of 3221 and 14:24 AEC next to one another. We also observed close the proximity of 3221 and 14:24 in the 1 bar PA processes.

Cation diffusion is required to form and dissolve 3221, and change the dominant AEC

Figure 6-12. SEM image (a) and EDS maps of elements Pb (b), Cu (c), and Ca (d) for OP-PA1 sample. Black particles A, C, and D are 14:24 AEC. Black particle B is 2:1 AEC. The gray regions e.g. are 2223. White streaks are 2212. Pb-rich phase 3221 are formed in the proximity to 14:24 AEC.
between 14:24 and 2:1AEC. As discussed early, 3221 formation could take place very rapidly and was complete in less than three hours at 783°C. The mass transport required in the PA processes could not be matched by solid-state diffusion. Rapid phase formation is a typical behavior of a liquid-assisted reaction. This suggests that 3221 may form from liquid. This liquid could be residual liquid left at the end of the OP-HT2 heat treatment or liquid that formed from partial melting of residual 2212 at elevated temperature in OP-PA1. It is generally believed that 2212 partially melts forming a transient liquid. That reacts with alkaline earth cuprates to form 2223. Converting liquid to 3221 and 14:24 AEC could reduce the amount of 2212 in the samples, which is reflected in the low 2212 SQUID index of 0.23 for OP-PA1 sample (Table 6-1) and high $H_k$ value of 700 mT. $H_k$ is believed to be determined by the residual 2212 content of the 2223 because flux pinning within the 2223 is weakened by those segments of the vortices that thread the residual 2212. A larger 2212 SQUID index indicates more 2212 in the sample. The lower 2212 the content, the higher $H_k$ is. On the other hand, converting residual liquid, which is most likely located at 2223 grain boundaries to crystalline 3221 and 14:24 AEC phases, cleaned 2223 grain boundaries and increased effective current-carrying areas, thus improving 2223 grain connectivity, therefore increased the glass vortex transition field $H_g$, which $H_g$ is believed to be determined by low voltage level dissipation of strong and sparsely distributed current obstructions. As shown in Table 6-1, the measurement results show that both $H_g$ and $H_k$ increased in OP-PA1 compared to OP-HT2 samples. When OP-PA1 samples were reheated to a higher temperature in OP-PA2, the 3221 dissolved and reformed liquid on heating. The reformed liquid may form crystalline phases including 2223 and 2212, or be left over as amorphous phase. The 2212 and
amorphous phases interrupt current paths and degrade 2223 grain connectivity. This caused the decrease in $J_c$ and irreversibility fields, as shown in Table 6-1.

Figure 6-13. MO images of (a) Q, (b) Q+PA, (c) SC, and (d) SC+PA samples taken by Dr. Polyanskii at University of Wisconsin at $T = 11$ K and $H=1200$ Oe (FC)
For both the monofilament and multifilament 2223 tapes, there were large differences in $I_c$ and $H_g$ between the Q and SC samples, and in particular significantly different increases in $I_c$ and $H_g$ for the Q and SC samples after the post anneal. There are three potential causes for these differences. One is that the quenching induced cracking in the quenched samples, and the cracks caused low $I_c$ and $H_g$ in the quenched samples. The second is there was more 2223 in the slow cooled sample than the quenched sample because the slow cooled sample had a 48-hour slow cooling step over a high temperature range of $774 \sim 822$ °C possibly suitable for forming 2223 formation. A larger amount of 2223 in the slow cooled sample resulted in a higher $I_c$ in the slow cooled compared to the quenched sample. The third one is that there was more residual liquid frozen in the quenched sample which coated the already formed 2223 grains in the quenched sample compared to the slow cooled sample. In the followings, evidence will be shown that the first two possibilities are unlikely and the third one is what occurs. This nonsuperconducting residual liquid blocked current flow in the sample and interrupted the connectivity, therefore causing significantly lower $I_c$ and $H_g$ in the quenched sample compared to the slow cooled sample. The PA cleaned the current barrier of residual liquid by converting it to crystalline phases, therefore enhanced $I_c$, $H_g$, and $H_k$. The increases in $I_c$, $H_g$, and $H_k$ were much larger in the Q+PA sample than the SC+PA sample because there was a larger amount of liquid coating the 2223 grains had been removed by the PA in the Q sample than in the SC sample.

Studies have shown that MO imaging is a reliable way to reveal defects, in particular cracks, in 2223 tapes, and the cracks are preferential places for flux penetration [7-9]. In the MO image, the flux-penetrated regions have different intensity compared to those regions without the flux penetration. Figure 6-13 shows the MO images of the Q, Q+PA, SC, and
SC+PA samples. There were not any sharp contrast regions seen in the MO images of the quenched and slow cooled samples except for the bright roof structures due to the 90° change of the flow direction of the induction current in the superconductor. This suggests that there were no cracks formed in the Q and Q+PA samples due to the thermal stress generated by the rapid temperature drop during the quenching. So the much lower $I_c$, $H_g$, and $H_k$ in the quenched samples compared to the slow cooled samples were not the result of the cracks.

To investigate what the consequence is for the $I_c$ if more 2223 formed due to a longer
anneal time as the sample SC sample had compared to the sample Q, an experiment shown in Figure 6-14a has been carried out. In this experiment, multifilament OX3849B samples were annealed at 822°C for 84 hours (That time is equal to the sum of the anneal time of 36 h at 822°C and the slow-cooling time of 48 h from 822°C to 774°C for the SC sample), and then quenched using the same procedure as the Q samples. This 84h-annealed sample followed by quenching was labeled as Q-84h. Figure 6-14b is the SEM image of the Q-84 sample, which shows that there was much more 2223 (gray regions) and less residual 2212 (white) in the Q-84 h sample compared to the Q sample (36h). However, as shown in Fig. 6-9b, the $I_c$ of the Q-84 h sample was 14 A, which was nearly the same as that of 13 A for the 36h Q sample. This indicates that the smaller 2223 content in the Q sample did not account for its lower $I_c$ compared to the SC sample. Table 6-2 lists the 2223 content of the Q, Q+PA, SC, and SC+PA samples evaluated by XRD. Even though the 2223 content did not change too much for the quenched samples after the PA, the $I_c$, $H_g$, and $H_k$ significantly increased in the Q+PA samples. This is further evidence that it is not a change in the 2223 content but something else occurring in the PA that improved the superconducting properties of the PA samples, especially the Q+PA samples.

Transient liquid that formed from 2212 or other sources reacted with AEC phases to form 2223 at elevated temperatures [10-19]. More 2212 should result in more liquid. So more liquid must form in the GT sample than HT1, IR, and FHT because the prior heat treatments in HT1 and FHT had already transformed most of the 2212 to 2223 and left behind much less 2212 in those tapes. There should be a considerable amount of liquid formed at 822°C in the CX9B and OX3849B GT samples before they were quenched or slow cooled to room temperature. Like other peritectic type reactions, the transient liquid in the conversion of
2212 to 2223 should continue to exist and surround the already formed 2223. In the quenching process (Fig. 6-1b and 6-14a), the 2223 formation was suddenly terminated by cooling the sample to room temperature. If the cooling rate is fast enough, the liquid was not allowed to convert to 2223 or 2212, instead, this transient liquid would be solidified as amorphous phases and coated on 2223 grain boundaries, where the liquid was originally located.

From the microstructural point of view, the striking characteristics that have been observed in the Q+PA and SC+PA samples were the formation of 3221 in the PA samples. The Q+PA sample had much larger amounts of 3221 than the SC+PA sample. If we look back to see what significant difference there was in the Q and SC samples, the answer was the amount of residual liquid. There was much more frozen residual liquid coating the 2223 grains in the quenched samples than in the slow cooled samples. The superconducting property improvement after PA can be explained by the removal of residual liquid by converting it to crystalline 3221 and AEC. A larger amount of residual liquid coating more 2223 grain boundaries was a serious current obstruction that blocked current paths and reduced the effective current-carrying area. This caused lower $I_c$, $H_g$, and $H_k$. The PA removed the residual liquid and cleaned current-obstruction by converting residual liquid to 3221 phases. This made the increases in $I_c$, $H_g$, and $H_k$ for both the quenched and slow cooled samples. Furthermore, there were a larger amount increases in $I_c$, $H_g$, and $H_k$ because a larger amount of residual liquid was removed in the Q+PA samples compared to the SC+PA samples. The few 3221 seen in the CX9B Q sample (Fig. 6-5) formed probably because the quenching rate was not fast enough to freeze all the liquid to amorphous phases. So some of the liquid was transformed to 3221 phase.
Table 6-2. The 2223 content in the quenched and slow cooled sample before and after post anneal is determined by XRD

<table>
<thead>
<tr>
<th>Samples</th>
<th>2223 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HT1</td>
</tr>
<tr>
<td>CX9B, Q</td>
<td>71</td>
</tr>
<tr>
<td>CX9B, SC</td>
<td>83</td>
</tr>
<tr>
<td>OX3849B, Q</td>
<td>80</td>
</tr>
<tr>
<td>OX3849B, SC</td>
<td>88</td>
</tr>
</tbody>
</table>

6.4 SUMMARY

Post anneal at a temperature of 783 °C and a total pressure of 148 bar increased $J_c$ (SF, 77K) of monofilament HT2 tapes from 34.6 kA/cm$^2$ to 41.3 kA/cm$^2$ and $J_c$ (0.1T, 77 K) from 13.7 kA/cm$^2$ to 16.8 kA/cm$^2$. The $H_g$ and $H_h$ were improved from 500 mT to 550 mT and from 580 mT up to 700 mT, respectively, in the OP-PA1 process. However, the $J_c$, $H_g$, and $H_h$ of the OP-PA1 samples dramatically decreased when the OP-PA1 samples were re-annealed at a higher temperature of 817 °C (OP-PA2). The 2212 SQUID index decreased in OP-PA1 and increased in OP-PA2. The striking microstructure features associated with the changes of $J_c$, $H_g$, and $H_h$ in post anneal processes were that Pb-rich 3221 phase formed in OP-PA1 samples and disappeared in OP-PA2 samples. The majority second phase was 14:24 AEC in the OP-PA1 sample, and 2:1 AEC in OP-HT2 and OP-PA2 samples. Residual liquid
converting to crystalline phases of 3221 and alkaline phases resulted in significant increases in $J_c$, $H_g$, and $H_k$.

Studies have been carried out to investigate the 3221 formation and its effects on the superconducting properties of the quenched and slow cooled 2223 tapes, in which the amount of preexisting residual liquid had been artificially changed, i.e., a larger amount of liquid was frozen in the quenched sample compared to the slow cooled sample. The SEM and XRD show that the Pb-rich phase 3221 precipitated in the quenched and slow cooled samples after a 3-hour post anneal at 783°C, whereas essentially no 3221 appeared in the quenched and slow cooled samples prior to the post anneal. For both monofilament and multifilament tapes, there were significantly larger amounts of 3221 found in the quenched samples compared to the slow cooled samples after the post anneal. The 2223 content was slightly increased in the post anneal.

The $I_c$, $H_g$, and $H_k$ were much lower in the quenched samples compared to the slow cooled samples. However, post annealing caused much larger increases in $I_c$, $H_g$, and $H_k$ in the quenched samples than the slow cooled samples. For monofilament CX9B tape, $I_c$, $H_g$, and $H_k$ were increased from 6.5 A, 48.2 mT, 190 mT in the quenched samples to 17 A, 203.9 mT, 575 mT, respectively, in the quenched samples after the post anneal, and changed from 20 A, 243 mT, 614 mT in the slow cooled samples to 24 A, 242.6 mT, 665 mT, respectively, in the slow cooled samples after the post anneal. For the multifilament OX3849B tape, the post anneal increased $I_c$ from 13 A to 24 A for the quenched sample, and from 24.5 A to 28.5 A for the slow cooled sample.

It was concluded that the 3221 formed from the residual liquid. A larger amount of residual liquid froze and coated the 2223 grains in the quenched samples compared to the
slow cooled samples, which accounts for the much lower $I_c$ in the quenched samples than the slow cooled samples. The PA removed the current obstruction - residual liquid - by converting it to crystalline 3221 phases, and thus enhanced the effective current-carrying area and improved connectivity. The removal of residual liquid resulted in improvements in $I_c$ of the post annealed samples. Because a larger amount of residual liquid had been removed so a larger fraction of grain surfaces were not covered by residual-liquid, post annealing caused significantly larger increases in $I_c$ in the quenched samples than in the slow cooled samples.

**REFERENCES**


CHAPTER 7. THROUGH-PROCESS QUENCHING STUDY OF 2223 TAPES

Chapters 5 and 6 show the post annealing (PA) significantly increased $J_c$, $H_g$, and $H_k$. The profound microstructure characteristics associated with the enhancement of electromagnetic properties are the formation of Pb-rich phase 3221. In the Chapter 6, the slow cooling and quenching experiments showed that 3221 came from residual liquid likely coated on the 2223 grains. The liquid removal resulted in better connectivity, and therefore higher $J_c$, $H_g$, and $H_k$. The next question that comes up is that when 3221 forms in the PA. In this chapter, through-process quenching has been carried out to address this question and to get in-situ visualization and better understanding of the PA process.

7.1 EXPERIMENTAL DETAILS

Through-process quenching experiments shown in Fig. 7-1 have been performed on the AMSC monofilament CX9B tapes after the initial rolling (green tape-GT) and the intermediate rolling (IR) fabrication stages, and the multifilament OX3162 tapes after the final heat treatment (FHT). All processing prior to the through-process quenching experiments were performed at AMSC. Samples 5cm long were cut from these tapes. Two types of quenching schedules were used, which are schematically shown in Fig. 7-1. One is for the CX9B GT samples (Fig. 7-1a), which is similar to that used in the quenched and slow cooled experiments discussed in Chapter 6 (Fig. 6-1b). The primary goal of this through-process quenching experiment was to continue addressing the issues about 3221 formation.
Figure 7-1. Schematic diagrams of the through-process quenching schedules for (a) CX9B GT, (b) CX9B IR, and OX3162 FHT. The major processing parameter difference between (a) and (b) is circled.

Chapter 6 focused on answering where 3221 the came from. The through-process quenching of CX9B GT samples emphasizes the issues when 3221 forms during the PA process and what impact the formation of 3221 has on the superconducting properties of 2223. In the CX9B GT through-process quenching, a higher maximum temperature $T_{\text{max}}$ of 830°C was used compared to that in Fig. 6-1b, which was to form more liquid at this higher temperature. Figure 7-1b is the same heat treatment used for 1bar and OP processing shown in Fig. 3-1b.

Applying the through-process quenching on the CX9B IR and OX3162 FHT using the heat treatment for 1atm and OP directly reveals what is occurring in the real 2223 producing. As
shown in Fig. 7-1, samples were quenched to room temperature from various points/temperatures in the process. The quenched samples were labeled using a combination of letter and temperature, in which the letter is in alphabetic order starting from “A” plus the temperature from which the sample was quenched.

The samples were cut from the AMSC CX9B GT, IR, and OX3162FHT tapes. The sample ends were sealed with Ag foil to prevent liquid from leaking out at high temperature. The samples were placed in a vertical quartz tube, which was externally heated. The top end of the quartz tube was sealed and the bottom end was dipped an oil bath. The samples were quenched by quickly dropping them into the oil bath. The I-V characteristics were measured using the standard four-probe technique in liquid nitrogen in magnetic fields up to 1 T applied approximately parallel to the c axis. Microstructure examinations were made using the JEOL 6100 and LEO 1530 SEMs. X-ray diffraction was performed on polished samples using a STOE diffractometer with Cu Kα radiation. The magnetic moment as a function of temperature was measured using a Quantum Design SQUID in a field of 0.5 mT applied along the longitudinal direction of the sample. The samples were reduced 30% in thickness by rolling before SQUID measurement of magnetic moment, and the crushed sample was zero-field cooled (ZFC) to 5 K in the SQUID measurements.

7.2 RESULTS

7.2.1 THROUGH-PROCESS QUENCHING OF CX9B GT
Figure 7-2 is the XRD patterns for the CX9B GT samples quenched at different points. The 3221 phase was first observed in sample F650 during heating in the PA. The amount of 3221 significantly increased at point J650 during cooling in the PA compared to the points F650 to I700. The 14:24 AEC was first seen at point I700. The amount of both 14:24 AEC and 3221 markedly increased at the J650 compared to the points from F650 to I700 (Note: The (240) peak of Sr-rich 14:24 AEC overlaps the (130) peak of 1:1 AEC).

Figure 7-2. XRD patterns of through-process quenched CX9B GT samples. The 3221 peaks are pointed out by dotted rectangular frame and the 14:24 AEC by dashed rectangular frame.
Figure 7-3. The evolution of $I_c$ (SF, 77K) and $I_c$ (0.1T, 77K) for quenched CX9B GT samples.

Figure 7-3 shows $I_c$ (SF, 77K) and $I_c$ (0.1T, 77K) for CX9B GT samples. It shows that the $I_c$ increased with decreasing temperature during the cooling in HT1. The $I_c$ (SF, 77K) and $I_c$ (0.1T, 77K) substantially increased from 13.2 A and 0.5 A for samples A830 to 33.6 A and 7.8 A for samples D467, but subsequently dropped to 19.3 A and 1.2 A for sample G783 when the temperature increased to the maximum PA soaking temperature of 783°C. The most striking observation was the $I_c$ (SF, 77K) and $I_c$ (0.1T, 77K) significantly increased in the PA soak at 783°C and subsequent cooling steps. The $I_c$ (SF, 77K) and $I_c$ (0.1T, 77K) increased to 41.4 A and 5.5 A for sample J650 compared to those of the sample G783.
Between sample J650 and sample K500, the $I_c$ (0.1 T, 77K) further increased to 9.6 A even though the $I_c$ (SF, 77K) did not go up. The PA increased $I_c$ (SF) and $I_c$ (0.1T) by 25% and 23% comparing samples D467 and K500.

Figure 7-4 shows the variations of $H_g$ and $H_k$ in the process. The $H_g$ and $H_k$ significantly increased from 49 mT and 168 mT for sample A830 to 165 mT and 440 mT sample D467, respectively. However, $H_g$ and $H_k$ went down rapidly when the temperature was raised in the heating steps between E and G. The $H_g$ and $H_k$ dropped from 165 mT and 463 mT for sample E500 to 48 mT and 182 mT for sample G783, respectively. The important observation was that $H_g$ and $H_k$ significantly increased during the 3-hour soaking at 783°C
Figure 7-5. (a) 2212 SQUID index and (b) 7K magnetic moment (emu) for quenched CX9B GT sample.

and also in the subsequent final cooling process. $H_s$ and $H_k$ were 185 mT and 450 mT for sample K500.
Figure 7-5 displays the 2212 SQUID index and the 7K magnetic moment for the quenched samples. The 2212 SQUID index represents the relative 2212 content in the 2223 and the 7K magnetic moment reveals the relative quantity of superconducting phases which includes 2223 and 2212. Both the 2212 SQUID index and 7K magnetic moment approximately increased from sample A830 to sample E500 except sample B782. They

Figure 7-6. Phase evolution of the CX9B IR samples quenched in the PA. The 3221 peaks are pointed out by dotted rectangular frame and the 2201 AEC by dashed rectangular frame.
Figure 7-7. (a) $I_c$ and, (b) $H_g$ and $H_k$ of quenched CX9B IR samples
decreased during the heating step of the PA (F and G), and then generally increased from sample G783 to sample I700, where the 2212 SQUID index and 7 K magnetic moment reached their maximum values. The 2212 SQUID index and 7 K magnetic moment went down from the point I700 to the point K500 with the lowest 2212 SQUID in the point J650.

Figure 7-8. Phase evolution of the multifilament OX3162 FHT samples. The 3221 peaks are pointed out by dotted rectangular frame and the 2201 AEC by dashed rectangular frame. All the peak intensities were normalized to the intensity of 2212 008 peak.
7.2.2 THROUGH-PROCESS QUENCHING OF CX9B IR AND OX3162 FHT

Figure 7-6 shows the phase evolution of the monofilament CX9B IR samples in the PA process. A large amount of 3221 was observed in samples H783, I700, J650, and K500. An interesting result is that 2201 was only seen in these samples that had lots of 3221, but was absent in samples without 3221. On examination, a very small amount of 3221 can be seen in sample G783. It is possible that 3221 nucleated prior to point G783 so 3221 grew during the soaking and cooling steps of the PA.

Figure 7-9. The 3221(300) and (111) peaks and the 14:24 AEC (240) peak for the quenched G-783 and H783 OX3162 samples. A much stronger 14:24 AEC peak was seen in the H783 sample compared to the G783 sample.
Figure 7-7 shows the results of transport I-V measurements for the CX9B IR samples. $I_c$, $H_g$, and $H_k$ for CX9B IR follow the same trends as those of the CX9B GT samples (shown in Fig. 7-3 and 7-4). $I_c$(SF, 77K), $I_c$(0.1T, 77K), $H_g$, and $H_k$ increased during the cooling of the high temperature annealing prior to the PA, decreased in the PA heating process, and increased during the PA cooling.

Figure 7-8 is the XRD results for the multifilament OX3162 FHT samples quenched during the PA process. A large amount of 3221 is seen in samples H783, I700, J650, and K500, after the samples had been subjected to the PA for 24 h at 783 °C. Figure 7-9 is a blow up from 30-32.5°C showing details of the 3221 and 14:24 peaks for samples G783 and H783.

Figure 7-10. The $I_c$(SF, 77K) and $I_c$(0.1T, 77K) as a function of the quenching points in the FHT process for the OX3162 FHT samples.
It clearly shows sample H783 had strong 3221 peaks whereas they were hardly seen in the sample G783. Moreover, the 14:24 AEC (240) peak in sample H783 was much stronger than in sample G783. This suggests that new grains of 14:24 AEC formed during the PA between sample G783 and H783. In fact, the 14:24 (240) peaks of samples H783, I700, J650, and K500 during or after the PA soak at 783 °C were larger than those of samples E500 and F660. The observation of the co-formation of 3221 and 14:24 AEC echoed those seen in the EDS mapping analysis in Chapter 6.

Figure 7-9 shows the $I_c$ variation of the OX3162 FHT samples. The changes of both $I_c$ (SF, 77K) and $I_c$ (0.1T, 77K) for the OX3162 FHT samples are similar to those of the CX9B IR and CX9B GT samples. The $I_c$ increased with decreasing temperature in the cooling step.
of the high temperature annealing before the PA, and decreased as the temperature was raised to the post annealing temperature. The $I_c$ did not change too much in the PA (between G783 and H783), but it significantly increased during the cooling in the PA. The $I_c$ (SF, 77K) of 170A and $I_c$ (0.1T, 77K) of 68A have been achieved in sample K500.

The $H_g$ and $H_k$ of the OX3162 FHT samples are shown in Figure 7-11. They varied in the same way as their $I_c$ did, i.e. the $H_g$ and $H_k$ increased with decreasing temperature in the cooling step after the 822°C heat treatment and decreased with increasing temperature in the heating step of the PA process. $H_g$ and $H_k$ increased during the soak (G783 to H783) at the maximum PA temperature.
Figure 7-12 shows the 2212 SQUID for OX 3162 FHT samples. The 2212 SQUID index increased during the initial cooling in samples A822 through E500. They decreased during the heating step of the PA, and then generally increased again starting from sample G783 to sample K500 except for sample J650, which had a low value.

7.3 DISCUSSION

7.3.1. 3221 PHASE FORMATION

3221 has been observed to form when the 2223 tapes underwent post annealing with a temperature lower than the maximum temperature used for HT1, HT2 or FHT. This does not matter that the starting materials are from the initial (GT), the medium (e.g. IR), or the end (e.g. FHT) stages of the 2223 oxide-powder-in-tube fabrication process. The XRD in Fig. 7-2 shows that 3221 formed at a temperature as low as 650°C at the heating step of the PA for the GT samples. The amount of 3221 significantly increased at the same temperature at the cooling step of the PA. This suggests that 650°C might be a crucial temperature for the 3221 formation. Vic Maroni at ANL [1] has shown that wetting liquid could continue to form at a starting temperature about 600°C in the Pb-rich BSCCO system. This may imply that 3221 precipitates from a liquid formed at a temperature around 650°C. A considerable amount of 3221 could form in a short time of 3 hour as shown in Chapter 6. The 3221 can form at a large range of temperature. As shown in Fig. 7-2, 3221 forms in the heating, soaking, and cooling steps of the PA. This further suggests that 3221 formation like the 2223 formation may be a peritectic rather than eutectic phase transformation, the latter is usually fixed at a certain temperature. Furthermore, as shown in Fig. 7-2, the side product of the 3221
formation includes the Sr-and Cu-rich 14:24 AEC [(Sr,Ca)$_{14}$Cu$_{24}$O$_x$]. This confirmed the co-appearance of 3221 and 14:24 AEC has been discussed in the Chapter 6.

For the FHT processed CX9B IR and OX3162 FHT tapes, most of the 3221 formed in the 24-hour soaking period of the PA at 783°C (seen in Figures 7-6 and Fig. 7-8). However, the XRD also shows that a small amount of 3221 had already formed at lower temperatures prior to the point G783. As shown in Fig. 7-8, a small amount of 3221 was observed in the sample F500 with a temperature of 500°C. The cooling down to and heating from low temperature of the FHT process was believed to be beneficial for the nucleation of 3221. For example, an experiment with the same schedule as shown in Fig. 7-1a without the cooling and heating steps has been performed on the AMSC multifilament OX3849B GT tapes to test the role of the cooling and heating steps. In this experiment, the samples went through the HT1 and cooled down to 783°C, and then directly held at 783°C for a 3-hour post annealing rather than further cooled and heated up to do the PA. It turned out that the $I_c$ of the OX3849B sample measured at the end of this process was 15A, which was much smaller than that of 24 A for the samples went through the cooling and heating steps. The SEM examination shows that a much smaller number of 3221 grains was found in the samples subjected to the non-cooling and-heating PA process than the samples undergone the PA process with cooling and heating steps. Similar observation was reported in other work [2]. All these evidently show that the cooling and heating steps in the currently employed PA process facilitated the 3221 nucleation, and the 3221 could form in a wide range of temperature down to 500~650°C.
14:24 AEC and 2201 phases were observed to form along with 3221. Figure 7-9 shows the amount of 14:24 AEC increased from the sample G783 to the sample H783, the amount of 3221 significantly increased in the latter. Furthermore, 2201 was observed in the samples H783, I700, J650, and K500 of both CX9B IR and OX3162 FHT, which had a large amount of 3221. However, no or miniscule 2201 was seen in the samples E500, F660, and G783 compared to the samples H783 through K500. This clearly shows that 2201 was another side product of the 3221. The existence of 2201 was also seen in the SQUID

![Image of magnetization moment as a function of temperature](image-url)

Figure 7-13. Magnetization moment as a function of temperature for rolled OX3162FHT G783 and H783 quenched samples obtained by SQUID magnetometer in a 0.5 mT magnetic field that was applied parallel to the long axis of the tape. The rolling reduction is 30%. The inset shows the low temperature region of M-T curves. The 2212 $T_c$ is defined as the temperature corresponding to the maximum height of the kink attributed by 2212.
measurement. Figure 7-13 plots the magnetic moment as a function of temperature for the OX3162 FHT G783 and H783 samples. On heating, there was a big increase in magnetic moment in the sample H783 at about 6–7K, which was attributed to the low $T_c$ 2201 phase, whereas there was no such jump in sample G783. It is obvious that there was a large amount of 3221 formed in the sample H783 and a miniscule amount of 3221 in the sample G783. The general composition of the 2223 material system has been shown to be kept constant during the formation of Pb-rich phase [3], the excess Cu after forming 3221 must be accommodated by other phases. So the Cu-rich 14:24 AEC should be the compensation phase for the rejected Cu in the formation of 3221. The 2201 forming along with the precipitation of Pb-rich phases was also observed by other researchers [3-4]. It is well accepted that the 2212 converts to the 2223 with the aid of a transient liquid, and partial substitution of Pb for Bi was found to promote the formation of liquid and enhance the formation and stability of 2223 [5-15]. Many researchers reported that the liquid formed from the reaction between 2201 and Pb-rich phase, this liquid reacted with the Pb-free 2212 to form Pb-doped 2212, and then the Pb-doped 2212 further reacted with AEC phases to form 2223 [6-12]. The 2201 present here is probably either the product of direct solidification of the transient liquid or the 2223 decomposition, the reversible reaction of Pb-doped 2212 and liquid (2201 + Pb-rich phase) forming 2223. Figure 7-13 shows that there was an increase in 2212 $T_c$ from sample G783 to sample H783, where the 2212 $T_c$ was defined by the temperature that corresponded to the maximum kink height in the plot of the magnetic moment as a function of temperature of the crushed sample obtained in the SQUID measurement, as shown in Fig.8-13. More detailed 2212 $T_c$ data will be discussed in the following section.
The 2223 could pick up oxygen when the temperature decreases during the cooling in the PA process. The $I_c$, $H_g$, and $H_k$ may be affected by the oxygen uptake in the cooling of the PA. Two experiments have been carried out to investigate the effects of oxygen content on the superconducting properties of 2223 tapes, in which the oxygen content was changed by changing either reaction atmosphere or annealing time. In one of these two experiments, shown in Fig. 7-14a, two AMSC multifilament 2223 tapes, OX3162 FHT and AP1057, were
subjected to a low temperature annealing at 500°C for 48 hours in three different reaction atmospheres consisting of oxygen and nitrogen (Fig. 7-14a). These reaction gas mixtures had 4%, 8%, and 100% oxygen content. In the other experiment, the OX3162 FHT samples repeated the heat treatment shown in Fig. 7-1b until 500°C in the PA cooling, then the samples were held at 500°C for 48 h and quenched down to room temperature. The corresponding sample was labeled as K500-48h. The oxygen content of the O₂-N₂ gas mixture used in the second experiment was fixed at 8%. Its detailed heat treatment is shown in Fig. 7-14b.

The results of I-V and SQUID measurements for the samples annealed at 4%, 8%,

<table>
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<tr>
<th>Oxygen content/sample</th>
<th>Ic (SF) (A)</th>
<th>Ic (0.1T) (A)</th>
<th>Hg (mT)</th>
<th>Hk (mT)</th>
<th>2212 index</th>
<th>2212 Tc (K)</th>
<th>2223 Tc (K)</th>
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<td></td>
<td></td>
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<tr>
<td>4% O₂</td>
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<tr>
<td>8% O₂</td>
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<td>477</td>
<td>720</td>
<td>0.48</td>
<td>79</td>
<td>109</td>
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<tr>
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<td>340</td>
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<tr>
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<td>650</td>
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</table>
and 100% O$_2$ are summarized in Table 7-1. It clearly shows that $I_c$ decreased with increasing oxygen content. $H_k$ did not change much by varying oxygen content. $H_g$ increased with increasing oxygen content for the AP1057 samples and did not change monotonically with changing oxygen content for the OX3162 FHT sample. As shown in Fig. 7-15, another striking result was that both 2212 and 2223 T$_c$ decreased with increasing oxygen content, which was consistent with the result reported by Morris et al. [15] that the increase in oxygen content depressed the T$_c$ of both 2223 and 2212. In this work, it is probably because the 2212 was oxygen overdoped and 2223 was oxygen-underdoped. Therefore, the oxygen uptake occurred in the PA increased the T$_c$ of 2223 and depressed the T$_c$ of 2212.

As shown in Table 7-1, the superconducting properties of the sample K500-48h with 48h annealing time did not change too much compared to the through-process quenched sample K500 with zero annealing time at 500°C. The sample K500-48h had higher $I_c$ (0.1T, 77K) but lower but $I_c$ (0.1T, 77K) than sample K500. There were small difference in $H_g$, $H_k$,
Figure 7-16. 2223 and 2212 $T_c$ of CX9B GT as a function of the quenching points.

Figure 7-17. 2223 and 2212 $T_c$ of CX9B IR as a function of the quenching points.
and 2212 SQUID index for the sample K500-48h and K500. The 2223 and 2212 $T_c$ is the same for these two samples. This experiment shows the uptake oxygen in the heat treatment may not the only reason accounting for the huge variations of superconducting properties with the temperature changes in the process.

An important and surprising result was found that the 2223 $T_c$ (onset) changed against the temperatures/points in the same way that $I_c$, $H_g$, and $H_k$ exactly varied with the temperature in the process. As shown in Figures 7-16, 7-17, and 7-18, the 2223 $T_c$ for all the through-process quenched CX9B GT, CX9B IR, and OX3162 FHT samples increased when the temperature decreased in the cooling step prior to the PA (from the point A830/A822 to the point D467/D500), and decreased in the heating step in the PA (from the point E500 to the point G783) and went up in the cooling step in the PA (from the point H783 to the point K500). The independent SQUID magnetic measurement (2223 $T_c$) and electrical transport measurement ($I_c$, $H_g$, and $H_k$) came to the same variation trends of superconducting properties. The more surprised finding was that the 2212 $T_c$ and 2223 $T_c$ changed with the process points in an opposite way, i.e., 2212 $T_c$ decreased from the point B782/B798 to the point D467/D500, increased from the point E500 to the point G783, and decreased again from the point H783 to the point K500. This implies that something happened during the cooling of process that was good for the 2223 $T_c$ and detrimental to the 2212 $T_c$, and the situation was reversed during the heating in the process, or something that was good for $T_c$ transported back and forth between the 2223 and the 2212 during the cooling or heating in the process.

Figures 7-6, 7-8, and 7-9 show that a large amount of Pb-rich 3221 phase formed between point G and point H for the monofilament CX9B IR and multifilament OX3162
Figure 7-18. 2223 and 2212 $T_c$ of OX3162 FHT as a function of the quenching points in the FHT process.

FHT tapes. The large amount of Pb present in the 3221 phase must come from somewhere inside the material system. The reaction that took place from point G783 to point H783 was the most unlikely process that would increase the Pb content in the 2223 and the 2212. Instead, it was plausible that the Pb content in 2223 and 2212 somehow depleted in the process from the point G to the point H. The Pb-doped 2212 single crystal work showed that the 2212 $T_c$ decreased with increasing Pb and oxygen content [16-20]. The oxygen content in 2223 and 2212 should keep constant or increase in the soaking process at 783°C for 24 h
from the point G to the point H. However, if the 2223 and 2212 $T_c$s were determined by oxygen content, as shown in Fig. 7-15 and Table 7-1, both the 2223 and 2212 $T_c$ should decrease with increasing oxygen content or change in the opposite direction if the oxygen doping state of 2223 and 2212 is different. So it should be the depletion of Pb in the 2223 2212 that caused the increase in the $T_c$ of 2223 and 2212 from the point G to the point H. On the other hand, it was reported that the 2212 $T_c$ decreased about 30 K (from 93 K to 65 K) when the Pb content increased from $x=0$ to $x=0.6$ in the 2212 single crystal with nominal composition of Bi$_{2.1-x}$Pb$_x$Sr$_2$CaCu$_2$O$_y$ [18]. If the Pb in the large amount of 3221 formed from the point G to the point H all depleted from the 2212 and 2223, much larger $T_c$ increase should have been observed. This suggests that the Pb in 3221 may also come from other sources. Many researchers have reported the partial substitution of lead for Bi in 2223 promoted the formation of a transient liquid to form 2223 [21-28]. As that have been shown in Chapter 6, most of the Pb in 3221 should come from this Pb-rich residual liquid, i.e. the residual liquid was converted to 3221 and other phases such as 2201, 14:24AEC, or other phases.

As discussed the opposite change in the trends of 2223 and 2212 $T_c$ in the cooling and heating steps of the PA process suggests the oxygen-doping state may be different. As shown in Fig. 7-18, the 2223 $T_c$ increased and 2212 $T_c$ decreased from the point H783 to the point K500. If 2212 was oxygen-overdoped and 2223 was oxygen-underdoped, 2223 $T_c$ increased and 2212 $T_c$ decreased due to the oxygen uptake during cooling. So $T_c$ change can be explained by the change of oxygen content during cooling. On the other hand, some of the Pb may be continuously depleted from 2223 to form 3221 and/or transfer through the transient liquid to 2212, which was observed to be able to accommodate more Pb as Pb-rich domains.
Figure 7-19. $I_c$ (0.1 T, 77K) as a function of (a) $H_k$ and (b) $H_g$ for the monofilament CX9B GT tapes, and $I_c$ (0.1 T, 77K) as a function of (c) $H_k$ and (d) $H_g$ for the multifilament OX3162 tapes.

[16], causing the $T_c$ increase in 2223 and decrease in 2212. The driving force for this process may be because the Pb is more stable as Pb$^{4+}$ in 3221 at lower temperatures than as Pb$^{2+}$ in 2223 [29]. This potential Pb transportation can be facilitated by Pb-rich transient liquid which was converted to 3221 and/or other phases including 2212, as the 2212 SQUID index increased during cooling (Fig.7-12). A similar process took place from the point A to the point D and opposite process occurred from the point E to the point G.
Figure 7-20. $J_c$ (0.1 T, 77K) as a function of $H_k$ for the multifilament OX3162 FHT tapes subjected to different processing.

The PA, especially the cooling steps removed serious current limiting mechanism of residual Pb-rich liquid by converting liquid to 3221 and other phases including 14:24 AEC and 2201, resulting in increased effective current-carrying area and improved connectivity, and thus significantly enhanced $I_c/J_c$. The $H_g$ and $H_k$ were also enhanced by removing strong current obstruction of residual liquid and introducing effective flux pinning defects/centers through changing cation concentration Pb doping. The situation was somehow reversed in the heating up step of the process due to the reformation of liquid and the change of Pb and oxygen doping in 2223. This resulted in the variations of $I_c$, $H_g$, and $H_k$ shown in Fig. 7-3, 7-4, 7-9, 7-11, and 7-12.
7.3.3. THE CORRELATION OF $I_c$ TO $H_g$, $H_k$, AND $T_c$

Even though the $I_c$, $H_g$, and $H_k$ varied in a wide range throughout the process for different 2223 tapes, it was found that the $I_c$ strongly correlated to the irreversibility fields.

Figure 7-21. $I_c(0.1 \, \text{T,} \, 77\text{K})$ as a function of $T_c$ for the (a) monofilament CX9B GT and (b) multifilament OX3162 FHT tapes.
As shown in Fig.7-19, there was a linear relationship between $I_c$ (0.1T, 77K) and $H_k$ for both CX9B GT and OX3162 FHT quenched samples. The $I_c$ (0.1T, 77K) linearly increased with increasing $H_k$. Figure 7-20 is the $J_c$ (0.1T, 77K) as a function of $H_k$ for OX3162 FHT samples that went through different processing. The removal of residual liquid and the change of cation doping caused the eventual increase in the $H_k$ and $J_c$ for the quenched and 1 bar processed samples. Extra enhancements of $H_g$ and $J_c$ have been achieved in the OP processed samples. 

Figure 7-22. (a) $H_k$ and (b) $H_g$ as a function of $T_c$ for the monofilament CX9B GT tapes, and (c) $H_k$ and (d) $H_g$ as a function of $T_c$ for the multifilament OX3162 FHT tapes.
samples due to elimination of additional current limiting mechanisms of cracks and porosity.

Figure 7-21 shows the $I_c$ (0.1T, 77K) as a function of $T_c$ for the through-process quenched CX9B GT and OX3162 FHT samples. It clearly indicates $I_c$ (0.1T, 77K) depended on the $T_c$. As discussed in the previous section, the involved processes that affected $T_c$ and $I_c$ were the conversion of residual liquid to 3221 and other phases and the change of Pb and oxygen doping. Figures 7-22 a & c show the well-defined linear relationship between $H_k$ and $T_c$ for the CX9B GT and OX3162 FHT quenched samples. The $H_g$ increased with increasing the $T_c$ in the range of 103 to 108 K for the CX9B GT quenched samples. The $H_g$ of OX3162 FHT samples slightly increased with increasing $T_c$ in the range of 106-109 K, and there was a big jump for $H_g$ at $T_c$ about 100 K. The connections between the irreversibility fields and $T_c$ may be reduction of strong current obstructions such as residual liquid and generation of effective flux pinning centers by change Pb and oxygen doping level.

7.4 SUMMARY

The XRD shows 3221 was first seen during the heating in the PA. The amount of 3221 significantly increased during the cooling step of the PA for CX9B GT tapes and at the PA soaking step for CX9B IR and OX3162 FHT tapes. The 14:24 AEC and 2201 were observed to form along with the 3221.

The $I_c$, $H_g$, $H_k$, 2223 $T_c$ (onset) increased during the cooling process prior to the PA, degraded during the PA heating, and went up again during the PA cooling. The 2212 SQUID index approximately followed the same trend as the $I_c$ change as a function of temperature in the process. However, $T_c$ for 2212 changed in the opposite way to the $T_c$ change for 2223.
Multiple reasons may attribute to the variations of $I_c$, $H_g$, $H_k$, $T_c$ with temperature in the process. The residual liquid that likely coated the 2223 grains was converted to crystalline phases such as 3221, 2201, and 14:24 AEC during cooling and reformed in the heating step. The residual liquid removed during cooling cleaned the grain boundaries and increased the effective current-carrying area, and thus enhancing $I_c$. During heating, the liquid reformed wetting the 2223 grain boundaries and degrading $I_c$. Alternatively, Pb-rich liquid solidification may decrease the Pb content in the 2223 and form more 2212 during the cooling. In addition, oxygen uptake may have enhanced the connectivity and flux pinning, and improving the $I_c$, $H_g$, $H_k$, and the $T_c$ of oxygen-underdoped 2223 and decreased $T_c$ of oxygen-overdoped 2212. The whole process was reversed in the heating step. Further systematical studies need to explore these complicated materials processes occurring in the 2223 processing.

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CHAPTER 8 GENERAL SUMMARY

Ag-sheathed 2223 conductor is the primary high temperature superconductor that has already had large-scale electrical demonstration applications. However, several major current-limiting mechanisms (CLMs) limit its performance. The overpressure processing of 2223 conductors has been developed to remove the CLMs of porosity, and cracks, and it had additional advantage of reducing 2212. These all enhanced the electromagnetic properties of 2223. The quenching experiments were carried out to get a better understanding of the role of residual liquid, which is another CLM, and the formation of Pb-rich 3221 phase in the post anneal process and its correlations to the superconducting properties of the 2223 conductors.

A flowing-gas overpressure system which is the first of its kinds used for the 2223 processing. This OP system allows the high-pressure Ar/O\textsubscript{2} gas mixture to be continuously replenished and maintains constant total pressure $P_{\text{total}}$ need to apply the isostatic pressure and oxygen partial pressure $pO_2$, which is crucial for forming 2223 pressure-processing.

The superconducting properties of overpressure processed 2223 tapes vary with the processing conditions. Optimum $I_c$ was found in the samples processed at the maximum temperature of $T_{\text{max}} = 822 \sim 824 \, ^\circ\text{C}$ while other processing parameters were kept unchanged. The mass density measurement showed that the 2223 filaments can be densified in OP processing at a total pressure $P_{\text{total}}$ as low as 50 bar. The maximum $I_c$ was attained in the OP samples processed in a total pressure of 148 bar. Further optimization of the total pressure may be needed.

The OP processing has been carried out as the final heat treatment for the 2223 tapes from different fabrication stages. The direct density measurements, and SEM and AFM images show OP processing effectively densified the 2223 ceramic filaments, removed
porosity, and healed cracks. OP processing significantly increased $J_c$ and enhanced the irreversibility field of 2223 tapes. Record $J_c$ (0.1 T, 77 K) of 30.8 kA/cm$^2$, $J_c$ (SF, 77 K) of 69.6 kA/cm$^2$, and $I_c$ (SF, 77 K) of 202 A have been achieved using commercial 2223 FHT tapes. An extrapolated zero-field $I_c$ (0 T, 77 K) of 235 A with $J_c$ (0 T, 77 K) of 90 kA/cm$^2$ has been obtained in the record $J_c$ 2223 tape. OP processing increased $H_g$ from 399 mT for the FHT sample and 409 mT for the FHT+1bar sample to 477 mT for the FHT+OP sample. The $H_k$ values of OP samples ranged from 650 to 765 mT.

Both SQUID and XRD measurements showed that OP processing reduced the 2212 content in 2223. The lowest 2212 SQUID index of 0.11 has been achieved in the OP samples.

OP processing improved 2223 connectivity. Magneto-optical current reconstruction indicated OP processed 2223 tapes had more uniform $J_c$ distribution, higher local $J_c$, a larger number of high $J_c$ local regions, and better connectivity than tapes that received identical 1 bar processing.

OP processing has been performed on the thermal slide heat treated (TSHT) 2223 tapes. It was found that adding IR to the TSHT samples prior to OP processing increased $J_c$, $H_g$, and $H_k$ for the samples with more 2212. SEM images of the samples after the IR deformation showed that IR densified the filaments, exposed the unreacted 2212, and formed a large number of cracks. This exposed 2212 may form transient liquid that reacts with AEC phases to heal the deformation cracks and further complete the 2223 formation. The size and distribution of 3221 precipitates was found to be relevant to the 2212 content and the IR deformation.
Post anneal at a temperature of 783°C resulted in significantly enhanced $J_c$ and improved irreversibility field. However, all these gains in $J_c$ and irreversibility field were lost when the PA samples were reheated and annealed at 817°C. The striking microstructure feature associated with the changes of electromagnetic properties was that 3221 phase formed in the PA samples and disappeared in the reheated samples. The 14:24 AEC phase was found to form along with 3221 in the PA. Studies have been carried out to investigate the 3221 formation and its effects on the superconducting properties of the quenched and slow cooled 2223 tapes, in which the amount of preexisting residual liquid had been changed by modifying the heat treatment. The SEM and XRD show that the PA generated a significantly larger amount of 3221 and larger increases in $I_c$, $H_g$, and $H_k$ in the quenched samples compared to the slow cooled samples after both sets of samples received a post anneal. The PA converted a larger amount of residual liquid, that likely coated on the 2223 grains, to 3221 and other phases in the quenched samples than in the slow cooled samples, which accounted for the larger increases in $I_c$, $H_g$, and $H_k$ in the quenched samples compared to the slow cooled samples. The 3221 formation strongly correlated to the residual liquid removal in the PA.

The XRD shows 3221 was first seen in the PA heating. The amount of 3221 significantly increased during the PA cooling for CX9B GT tapes and during the PA soaking step for CX9B IR and OX3162 FHT tapes. The 14:24 AEC and 2201 were observed to form along with the 3221. The $I_c$, $H_g$, $H_k$, 2223 $T_c$ (onset) increased during the cooling process prior to the PA, degraded during the PA heating, and went up again during the PA cooling. The 2212 SQUID index approximately followed the same trend as $I_c$. However, $T_c$ for 2212 changed in the opposite way to the $T_c$ change for 2223.
Multiple reasons may attribute to the variations of $I_c$, $H_g$, $H_k$, and $T_c$ with temperature in the process. The residual liquid that likely coated the 2223 grains was converted to crystalline phases such as 3221, 2201, and 14:24 AEC during cooling and reformed in the heating step. The residual liquid removed during cooling cleaned the grain boundaries and increased the effective current-carrying area, and thus enhancing $I_c$. During heating, the liquid reformed wetting the 2223 grain boundaries and degrading $I_c$. Alternatively, the Pb-rich liquid solidification may decrease the Pb content in the 2223 and form more 2212 during the cooling. In addition, oxygen uptake may have enhanced the connectivity and flux pinning, and improving the $I_c$, $H_g$, $H_k$, and the $T_c$ of oxygen-underdoped 2223 and decreased $T_c$ of oxygen-overdoped 2212. The whole process was reversed in the heating step. Further systematical studies need to explore these complicated materials processes occurring in the 2223 processing.
APPENDIX PUBLICATIONS AND PRESENTATIONS

RESEARCH-RELATED PUBLICATIONS


RESEARCH-RELATED ORAL AND POSTER PRESENTATIONS


