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Processing Issues of Bi2Sr2CaCu2O8 Round Wire Involving Leakage and Alumino Silicate Insulation

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PROCESSING ISSUES OF Bi$_2$Sr$_2$CaCu$_2$O$_8$ ROUND WIRE INVOLVING LEAKAGE AND ALUMINO SILICATE INSULATION

By
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This work is dedicated to:

My parents, for the sacrifices they have made to provide me with a worry free, endless environment of learning. Your continual support in each of my endeavors has provided me with a limitless future.

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ABSTRACT

A major issue seen in Bi$_2$Sr$_2$CaCu$_2$O$_8$ (Bi-2212) conductor was leakage from the liquid within the wire during the partial (peritectic) melt. The leakage in the wire was the main focus of this work initially. By examining leaked wire, cracks along the length of the wire were found in several leakage regions. Green wire, which has not been heat treated, was examined for the presence of the same longitudinal cracks found in leaked wire. These defects were covered in yttria, which is non-reactive with Bi-2212, to wick out liquid through surface defects that might occur. After the samples were heat treated, some of the cracks exhibited leakage. The longitudinal cracks, caused during the manufacturing processes, were the source of the leaks. The processing parameters were changed by the wire manufacturer to ameliorate the cause of leakage, in parallel with this study, and the new wire does not have the same leakage problem as the preceding wire. Due to the issue of leakage being solved by the wire manufacture, the study ended.

Insulation is used to separate the wire to prevent bonding at high temperatures. The insulation reacts with the surface of the wire leaving behind large sections stuck on the conductor and forming a glassy phase after the reaction. The alumino silicate fiber composition consists of crystalline alumina and amorphous silica. The fiber reacts with the wire by sticking to the surface. Different compositions of these compounds were tested against Ag using a line of 3M NEXTEL fibers and pure SiO$_2$. Any amount of amorphous silica causes a reaction with Ag; however, pure amorphous silica does not have a reaction, but due to the ease with which it is contaminated with salts, which causes it to react with Ag, its use is currently not recommended. The insulation also has an effect on performance by decreasing $I_c$ by 20%. Ag wire was wrapped around insulation to provide surface contact between the insulation and conductor to show this decreased performance in short side-by-side samples and along a length of wire. Although flux pinning is the same between insulated and bare samples, the connectivity is affected by insufficient grain growth. Cu was lost from the Bi-2212 core into the insulation. The loss of Cu to the interface of Ag and the braid causes a change in
phases by creating an excess of secondary phases and pores and decreases the total density of the filaments. Cu loss is the mechanism behind the loss in $I_c$. 
CHAPTER 1
INTRODUCTION

The main focus of this work was to investigate processing issues of the superconductor Bi$_2$Sr$_2$CaCu$_2$O$_8$ (Bi-2212) that develop during the high temperature heat treatment. Bi-2212 is a promising conductor because of its ability to carry high current in the presence of high magnetic field and its ability to be fabricated in round wire geometries. The superconducting round wire is used to make coils and coil insert and many issues developed when going to long lengths of wire wrapped onto coil formers. The conductor's strain sensitivity requires the coils to be wrapped before the heat treatment so the turns of the conductor are in close contact during the high temperature heat treatment, which requires insulation to prevent bonding. The issues that this thesis deals with are leakage and reactions with alumino silicate insulation that occur during the heat treatment. Before getting into the motivation for this work, this chapter will briefly cover the concept of superconductivity, the rise of cuprate superconductors, and the basics of Bi-2212.

1.1 Superconductivity

![Phase Diagram](image)

**Figure 1.1**: Phase Diagram showing the superconducting envelope. The region bounded by each sheet represents the conditions needed to have superconducting properties; temperature, current, and field. The maximum critical parameters are noted as $T_c$, $J_c$, and $H_c$. 
Superconductivity is a phenomenon found in materials that results in frictionless flow of electrons. The phenomenon occurs only in a few specific materials and is exhibited only when the material is within an envelop of three variables: Temperature, Current Density, and Applied Field\(^1\) (Figure 1.1). When below the threshold values of these variables, moving electrons in the lattice distort the positive network creating localized positive clusters following the moving electron. These positive clusters attract a separate negative electron, binding the two electrons over a coherence length\(^2\). These pairs of flowing electrons are known as Cooper pairs and flow as a Bose liquid (superfluid)\(^3\) with a quantized excitation energy to cause motion. Using this phenomenon, the electricity flowing through the superconductor does not lose any energy and can flow in a closed loop essentially forever.

Frictionless electricity has opened the doors for many applications over the past few decades. Magnetic Resonance Imaging (MRI) machines have become commonplace in hospitals across the country and owe their success to superconductors providing a high and even magnetic field surrounding the patient. Magnetic Levitation (MagLev) trains levitate using superconductors to achieve speeds in excess of 500 km per hour without any of the vibrations felt through conventional wheels. Superconducting toroids are used to contain plasma within nuclear fusion reactors so that the power of the Sun can be harnessed on the surface of the Earth. Particle accelerators that use superconducting magnets and superconducting magnet inserts made out of materials like Bi-2212 cause collisions between subatomic particles traveling at speeds nearing the speed of light in order to study the very building blocks of the universe. All of the superconductors in these devices need cryogens to operate below their superconducting transition; however, science continues to push for superconducting properties in materials closer and closer to room temperature (RT) with homogeneous field and high current carrying capabilities.

1.2 Cuprate Superconductors

Prior to 1986, no superconductors with a transition temperature above 23 K had been discovered. In that year, Bednorz and Muller discovered a cuprate perovskite ceramic with a critical temperature \(T_c\) of 35 K\(^4\). The compound, Ba\(_2\)La\(_{5-x}\)Cu\(_5\)O\(_{5(3-y)}\), was the first high temperature superconductor and opened the doors for several other cuprate conductors to be
developed over the next few years. The following year saw $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with a normal transition of 40 K$^5$. Soon after, YBCO and BSCCO materials were developed with $T_c$ of 93 K$^6$ and 107K$^7$ respectively. The discovery of YBCO and BSCCO allowed superconductivity to take place above the temperature at which nitrogen liquefies. Since liquid nitrogen is created commercially and is inexpensive, it would allow these new superconductors to use it as a cryogen instead of the costly liquid helium. Although more materials have been developed, some with higher $T_c$$^8$$^9$. YBCO and BSCCO have remained at the forefront of the high temperature superconductor (HTS) development.

1.3 BSCCO

BSCCO refers not to a single material system but rather a family. The initial discovery of BSCCO was realized with a composition of BSCCO referred to as Bi-2223$^7$. The name is derived from the stoichiometry of the superconducting phase, $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$. 2223 is created in tapes, which is a less desirable geometry than wires because much of the electrical designs used today rely on wire architecture. It took only a year after the Maeda et al.’s discovery before Heine et al.$^{10}$ developed a slightly different composition of conductor and a completely different way to manufacture them. Precursor oxide powders can be mixed and calcinated before being densely packed in a hollow Ag billet and extruded into wire creating a powder in tube (PIT) processing technique, seen in Figure 1.2. This PIT process creates lengths of wire in a round geometry that can be kept round or rolled flat. The wires are heat treated through the peritectic melt (partial melt processing) and upon cooling, the superconducting phases are created. The superconducting phase in this new wire has a composition of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$, which is referred to as Bi-2212.
Both compositions of BSCCO carry current in a similar way. For the explanation in this paper, the unit cell for Bi-2212 is used (Figure 1.3). The unit cell of this conductor has two distinct types of layers. The first is the conducting layer containing \( \text{Cu}^{2+} \) and \( \text{O}^{2-} \). There are two of these layers held in place by a layer of \( \text{Ca}^{2+} \). The electrons flow on these Cu-O planes below the critical temperature. The second is the binding layers made of Sr and O, and Bi and O. It is these layers that contain the source of the charge required for the conduction band. The binding layers allow \( \text{Cu}^{2+} \) to release an electron, creating electron-hole pairs in the conduction layer\(^{12} \).
1.4 The Heat Treatment

Partial melt processing is the heat treatment that brings the wire above the peritectic melt in order to melt the precursor powder. The formation of Bi-2212 in wire form happens after a partial melt heat treatment. A standard heat treatment regime has been adopted by several different research institutions and companies alike, but the actual temperatures may vary. The heat treatment process has four distinct regions as shown by Hellstrom\textsuperscript{11} and can be seen in Figure 1.4. Melting is the first region and follows the heat treatment from beginning to after the peak temperature. The first steady temperature anneal prevents pressure build up in the conductor by allowing the $O_2$ release right below the melting temperature of Bi-2212\textsuperscript{13}. When at peak temperature, the conductor has three phases; $(Sr, Ca)_{14}Cu_{24}O_x$ known as 14:24 alkaline earth cuprate (AEC), $(Sr, Ca)_{9}Cu_{16}O_x$ known as Cu free (CF), and liquid. As peak temperature varies, the size of the secondary crystalline phases increases\textsuperscript{14}, which is not desirable. Extended amounts of time at peak temperature can have similar results, so this parameter is kept short. The second region is the formation and aligning of Bi-
The formation of Bi-2212 occurs during the slow cool regime and is dependent on the cooling rate, which occurs roughly 870°C for a 2.5°C/hr cooling rate used.

**Figure 1.4**: General heat treatment profile used for Bi-2212 round wire. The heat treatment has four regions that take the conductor through the partial melt region and reform Bi-2212 on cooling.

Bi-2212 consumes all three phases in order to form (Equation 1.1). Smaller grains are more desirable for growth because they minimize the diffusion distance, have greater ability to react for a given time, and do not inhibit the growth of large grains of Bi-2212\textsuperscript{11, 16}. When the diffusion path is limited, liquid is trapped in-between two formed Bi-2212 grains, so the peritectic reaction is incomplete on cooling and Bi\textsubscript{2}Sr\textsubscript{2}CuO\textsubscript{x} (2201) forms, which is a non-superconducting phase and is not desired\textsuperscript{16}. After the formation of Bi-2212, the third region involves a long term anneal to maximize the formation and alignment of Bi-2212\textsuperscript{11}. This stage is necessary for high performance but the mechanisms causing change in this stage are not known. Lastly, the final region is a cool to room temperature\textsuperscript{11}. This final stage allows for more oxygen uptake and an increase in carrier density of the conductor\textsuperscript{15}. The wire is then fully processed. It is after the heat treatment that two problems are seen. Fully heat treated coils have black spots on the surface, signs that the liquid within the wire has escaped to
the surface. The insulation sticks to the surface which shows signs of a reaction. Each of these may be responsible for the loss in performance seen between coils and short samples of the same wire.

1.5 Leakage

Leakage refers to the loss of liquid from the inside of the conductor that would later become Bi-2212. The powder in the conductor must undergo the partial melt heat treatment in order to create the Bi-2212 within the wire. Assuming the Bi-2212 that would have grown would have carried current, leakage represents a loss in critical current density ($J_c$). When short samples are tested, the ends are sealed and the wire is heat treated. If the ends are not sealed, the liquid melt is able to escape via the open ends during the partial melt. In coils, the ends of the wire play less of a role but are still sealed. When coils were heat treated, black spots, containing all four constituents from within the wire, Bi, Sr, Ca, and Cu, appeared frequently but sporadically across the surface of the wire which can be seen in Figure 1.5. If the coil was multilayered, the spots appeared on all of the layers. The source of these spots was the liquid from within the wire when the wire was in the partial melt phase. Leakage is a huge obstacle for Bi-2212 not only because it produces an ugly coil but it also presents major doubt in the homogeneity of the wire along the length of a coil. The losses in performance in coils versus short straight samples could be due to the leakage in the coil.
Figure 1.5: A small coil of Bi-2212 with black spots within the insulation. The spots are liquid that has escaped the wire during the partial melt. This image is courtesy of U. Trociewitz.

The causes of leakage must have an effect on the wire during the peak temperature of the heat treatment. Improper deformation during the drawing process causing pinhole and other surface defects was thought to be the leading cause of leakage. Pinholes provide a channel for the liquid to escape the conductor and inclusions of other materials could affect the local melting temperature. Surface defects are not the sole possible cause. Figure 1.6 (a) shows work done by Jianyi Jiang where he observed the surface of the conductor after heat treatment and documented large amounts of alumino silicate insulation sticking to the surface\textsuperscript{17}. The reaction between the Ag and insulation presented another possibility to investigate.
1.6 Insulation

The insulation is used on the conductor to prevent bonding between the turns of wire in contact with one another during the heat treatment. The alumino silicate braid has a composition of 73/27 wt% $\text{Al}_2\text{O}_3$-$\text{SiO}_2$ with crystalline alumina and amorphous silica phases. After heat treatment, the insulation sticks to the surface of the conductor forming a repeating pattern (Figure 1.6 (a)). The sticking insulation mimics the braid, sticking to the Ag where an individual bundle of the braid was in direct contact with Ag. An interaction between these surfaces is known to be taking place and the extent of this interaction was a focus of this work.

The insulation has more than just a local impact on the surface of the conductor. Whenever a coil is heat treated, two straight samples, called witness samples, accompany the coil. The two straight samples are roughly 7 cm long but only one is insulated. When $I_c$ is measured, the bare witness serve as a base line for the level at which the coil should perform. The $I_c$ of a coil is roughly 60-70% less than the bare witness sample. The loss was always thought to be an issue of length dependence or interactions with the coil former. The insulated witness sample was used to see if insulation has an effect on the performance of the witness samples. Figure 1.7 shows the performance of insulated straight samples is roughly 18% less than the bare witness samples of the same length. This represents a portion of the total loss felt by coils just through the use of tightly wound insulation.
Figure 1.7: Performance loss between bare and insulated witness samples. The right graph is the current ($I_c$) of the insulated wire normalized to the $I_c$ of the bare counterpart. The loss is roughly 18%. Data from a variety of witness samples for testing coils and other process parameters.\textsuperscript{18-20} All samples are approximately the same length.

The loss of current carrying capability in insulated samples may be due to many factors; mechanical strain, oxygen diffusion, and chemical reactions. The insulation on the surface of the conductor reacts at high temperature and the thermal contractions may be different so on cooling strain could develop in the conductor that could affect the performance. Looking closer at the insulation, sticking fibers reacted together to form a glassy phase and the fibers fused together. Propagation of a crack through multiple fibers suggests that the fibers act as a single material (Figure 1.6 (b)). Oxygen doping may be inhibited due to this glassy phase affecting a large portion of the surface. Since the insulation is reacting in some way, chemical interactions between the braid and constituents of the wire remain a possibility. A loss of any constituent from the Bi-2212 core would cause a change in the overall composition during the heat treatment, causing differences in performance. The ways that the insulation affected the conductor was investigated in this work.
CHAPTER 2
EXPERIMENTAL SETUP

2.1 Equipment and Processes

2.1.1 The Conductor

All of the wire conductor used for these experiments were manufactured by Oxford Superconducting Technology, New Jersey. The batch numbers of conductor are indicated in the specific experiment. The batch numbers are the date at which the billet was created, starting with the year. Sometime during 2005, Oxford changed the processing parameters used to create their wire, which lead to a distinction between old generation and new generation wire (See Section 4.1.2 for more details). Table 2.1 provides the generation of the conductor used in each experiment, if known.

<table>
<thead>
<tr>
<th>Batch Number</th>
<th>Generation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pmm 021212-2</td>
<td>unknown</td>
</tr>
<tr>
<td>pmm 011127-2</td>
<td>unknown</td>
</tr>
<tr>
<td>pmm 050831</td>
<td>Old</td>
</tr>
<tr>
<td>pmm 070601-1</td>
<td>New</td>
</tr>
<tr>
<td>pmm 070413-4</td>
<td>New</td>
</tr>
<tr>
<td>pmm 070420-4</td>
<td>New</td>
</tr>
</tbody>
</table>

More detailed information is provided here about the conductor used to examine the effect of insulation on the conductor. The multifilament Bi-2212 round wire was manufactured using the powder-in-tube process with a batch number of pmm 070413-4. The wire contains a total of 595 filaments (85 filaments in a bundle and a total of seven bundles (Figure 2.1)). The
Ag surrounding the filaments is pure Ag while the sheath material is a Ag-Mg alloy. The composition of the precursor powder is Bi$_{2.17}$Sr$_{1.94}$Ca$_{0.89}$Cu$_{2.00}$O$_{x}$. The diameters of bare and braided conductor are 1.06 mm and 1.30 mm respectively. The filament diameter and filament spacing are $\sim$20 $\mu$m and $\sim$15 $\mu$m respectively. The fraction of superconducting material in the cross section is $\sim$25%$^{15}$.

2.1.2 The Heat Treatment

The heat treatment (Figure 2.2) used for these samples follows the same pattern as described in Chapter 1.4, but the temperatures and ramp rates are included here. The first ramp is 160°C/hr up to 820°C. The 820°C anneal is maintained for 2 hours, followed by a 50°C/hr ramp up to peak temperature. The peak temperature used is 890°C and it is maintained for 12 min. The first cool goes to 880°C in 60 minutes followed by a 2.5°C/hr cooling rate until it reaches 835°C. The 835°C anneal is maintained for 24 hours, followed by a furnace cool.
2.1.3 Quench Furnace

The quench furnace is a furnace that is mounted in a vertical position. The furnace is made from a ceramic tube wrapped with Kanthal wire to provide a heating element. The ceramic tube is wrapped in an insulating fiberglass material, followed by aluminum foil. The entire furnace is supported with a metal scaffold sandwiched between a pair of approximately 30 cm circular metal disks and held together with metal thread rod as seen in Figure 2.3. Other clamps are used for support and are attached to the threaded rod sticking out past the circular metal disks. The entire rig is placed on top of a board that has a square hole smaller than the size of the metal disks so that the furnace can be supported by the board. There are four smaller holes for the thread rod to extend through. A quartz tube 4.75 mm ID and 5.00 mm OD, sits in the ceramic tube and extends out from the furnace roughly 10 cm from each side. The quartz tube has four small quartz tubes inside that have been fused inside. These four smaller quartz tubes have a 1.7 mm ID and a 1.9 mm OD and extend from 1 cm above the center of the furnace to roughly 5 cm to the top of the large quartz tube. The smaller quartz tubes provide sample tubes for the quench studies (Figure 2.3 (c) and (d)), so that each sample is not affected by the falling of adjacent samples.
Figure 2.3: Components of the quench furnace. (a) Schematic of the quench furnace. (b) Image of quench furnace. (c) Schematic of furnace sample tubes. (d) Image of furnace tubes.

The large quartz tube has two brass caps that provide specific purposes for each end. Both the top and bottom end cap have cooling water tubes wrapped around it to prevent the end caps from reaching high temperatures. The water is supplied by a faucet located in a fume hood nearby. Both have a port for \( O_2 \) gas, where the flow enters the top at 1 bar, flows past the sample and exits at the bottom of the tube into a beaker of water for visual signs of gas flow. The \( O_2 \) is provided via a compressed gas cylinder outfitted with a gas regulator at the mouth of the cylinder followed by a flow meter. The top cap has a feed through for a thermocouple and the current leads that are needed for the quench. Four pairs of wires are attached to four terminals on the outside of the cap and connect the cap to a trigger box. The trigger box can select which pair of wire to send a large amount of current through. Inside the cap are four pairs of rods. Each pair of rods is bridged by a hanger made from new wire for
each run (See Section 2.1.4). The hanger wire is deformed and measured for each test sample. When the current is triggered from the trigger box, the small diameter wire that bridges the two rods inside the cap is burned out, and the sample that it holds is able to fall freely through the quench furnace into a brine quench fluid. Since there are four pairs of rods, four separate quenches can be conducted with each furnace run.

The bottom cap is left open and is inserted into a large beaker of quench fluid. Based on the work done by T. Shen, the quench fluid that works best for the conductor is brine\textsuperscript{15}. The samples fall into the quench solution and then are removed quickly from the salt water so that the long term effects on the conductor are eliminated.

The furnace is driven by a Yokogawa temperature controller model UP25. This unit has the ability to program the entire heat treatment, so that the furnace is completely automated once the program is selected. It was programmed with the standard heat treatment.

2.1.4 Quench Furnace Sample Mount Assembly

The quality of the quench is dependant on the quality of the sample mount assembly. The job of the sample mount (Figure 2.4) was to hold the sample and to bridge the gap between the pair of rods at the top and the hot zone of the furnace. The sample mount was made of Omega Engineering nicrome wire and a small piece of inconel to provide weight. Although slight variations were used, the basic mount explained here is representative. Roughly a meter of wire was folded in half so that the center became a loop. From this loop, the wire was twisted on itself up the entire length then pulled in tension until it yielded resulting in a straight section across its entire length. The end of the mount farthest from the loop was curled to make a hook. The small piece of inconel was attached by wrapping it with two lengths of wire just above the loop to provide weight when the quench was initiated. The sample was then hung on the loop using insulation (Figure 2.4 (d)). New insulation was used for every quench. The top of the sample mount was connected to a hanger, seen in Figure 2.4 (c). The sample mount and hanger a fixed length so the Bi-2212 wire sample was in the hot zone in the furnace. The hanger was made from the same wire, bent into a “V” shape so that the sample mount hook would sit in the base of the “V”. The top of the hanger was bent at right angles and given small hooks. The hooks are placed around the rods inside the top brass cap,
described in Section 2.1.3, and bridged a single channel, by completing the circuit between the two small rods seen in Figure 2.4 (c). One sample mount was loaded into each of the four small quartz tubes. Once the cap was lowered onto the large quartz tube, the samples were ready to be heat treated.

![Image of sample mount assembly with labels:](image)

**Figure 2.4:** Components of the sample mount assembly. (a) Schematic of the sample mount assembly. (b) Image of the sample mount assembly. (c) The hanger bridges a pair of rods to complete the channel and gives a place for the sample mount to hang. (d) Samples attached to the sample mount with insulation.

2.1.5 Lindberg Blue Furnace

The Lindberg M Blue furnace (Figure 2.5) was used to heat treat the striped samples. The furnace is a three zone furnace with a primary controller and two slave controllers. The Lindberg controller governs all three zones but adjust for variations from three separate thermocouples, one in each zone. The furnace is also fully automated once it is programmed.
The samples were placed inside an alumina oxide boat and placed in the hot zone. Gas flow of oxygen was supplied by an in-house distribution system.

![Lindberg Blue furnace and temperature controller.]

**Figure 2.5:** Lindberg Blue furnace and temperature controller.

### 2.1.6 Multi-Sample Probe 3 (MSP3)

MSP3 (Figure 2.6) is a probe used to measure $I_c$ across samples at 4.2 K and at 5 T. It is used in conjunction with a 5 T magnet and a data acquisition program called Labview. The probe is roughly 1.2 m long and has square copper rods that bridge the length from the leads at the top to the samples at the bottom. The probe has the ability to measure 8 samples in one batch. Each sample is soldered across two copper leads. Due to the short length of the samples, a superconducting bridge was used in order to allow the samples to reach the leads. Voltage taps are placed from 10-15 mm apart on the middle of the samples and the separation was recorded in the data acquisition software. The resistance of the samples is checked to ensure a good connection. The probe is precooled with liquid nitrogen and inserted into a vertically oriented 5 T superconducting magnet. When the probe is in place, the magnet is filled with liquid helium. The sample is also submerged in liquid helium. The magnet is ramped up to field after the magnet is cooled to 4.2 K. Once the magnet is at field, measuring the samples begins.
Figure 2.6: MSP3 schematic and images. The current leads at the left are attached to the Cu rods that extent down to the sample holder on the right. Current is ramped through each sample to measure the where the sample transitions back to its non superconducting state.

The positive current leads from all samples holders are shorted together and the negative current lead is attached to the channel corresponding to the sample being measured. A current is ramped through the sample while the data acquisition software collects voltage measured across the sample. The resulting plot graphs current as the independent variable against electric field. The electric field is calculated from the voltage tap length and measured potential. Ultimately, the plot shows the change in resistance as a function of applied current.

A criterion of $1 \mu V/cm$ for $I_c$, where $I_c$ is the critical current, or the maximum amount of current that can flow through a conductor before it transitions into the normal phase. The critical current $I_c$ can also be referred to current density, $J$ or $J_c$ (Equation 2.1). The software allows the user to manipulate a baseline and trend line in order to determine an $n$ value and the $I_c$.

The transition is exponential and has an $n$ value, (Equation 2.1) which is used to describe the sharpness at which the transition occurs.

$$E = \alpha J^n$$

Equation 2.1

\cite{21}
2.1.7 Standard Microscopy Preparation for SEM

In order to view the microstructure using the SEM, the samples need be prepared in a way to expose the surface or cross section of interest. This section will outline the standard method used to prepare these samples.

Approximately 6 g of Extec Carbon Conductive Mounting Compound was measured and placed into the Buehler Simplimet 3000 Automated Mounting Press. The mounting press achieved a pressure of 4000 psi for 5 minutes and was cooled for 3-4 minutes. The resulting puck was then removed from the press and modified in order to be a holder for each set of samples. For wire, drilling holes into the puck is sufficient. For anything more complex, the specifics modifications for each sample set can be seen in the following sections for the samples in question.

After the samples were placed in the modified puck, they had to be secured in the puck by melting more mounting compound to fill the gaps. 6-10 g Carbon Conductive Mounting Compound was measured and placed into a coffee grinder and ground for a minute. This reduced the particle size of the powder and allowed it to flow into the spaces between the sample and the puck and to allow quicker melting of the particles once in the mounting press. The mounting press was preloaded with the puck holding the samples. The cylinder was lowered and the new fine powder was added to the top. The Automated Mounting Press then achieved the same conditions as before. This resulted in a solid cylindrical puck with the samples locked in the puck.

The samples were then subject to a grinding process to expose the desired cross section. Many different steps were used to achieve the desired outcome. This process was done on Buehler Ecomet using different grades of sandpaper. Samples were dry ground using 320, 400, 600, and 800 grit paper. A sample would not graduate to the next grit until the sample was viewed under an optical microscope and the scratches from the previous grit had been removed. The samples were then placed on a Vibromet 2 Vibratory Polisher for several hours and checked every hour for over polishing. The Vibromet had Mastertex cloth and a mixture of 0.05 μm Al₂O₃ in ethanol. The amplitude was set at 10%. This specific model only
has horizontal vibrations. The samples were then cleaned of \( \text{Al}_2\text{O}_3 \) using ethanol and Kim Wipes and checked under an optical microscope for contamination.

The polished samples were viewed with an optical microscope and a Carl Zeiss 1540 Scanning Electron Microscope (SEM). The chemical composition was measured using energy dispersive spectroscopy (EDS).

2.2 Leakage

It was hypothesized that leakage was due to pinholes or other surface defects on the wire caused during the fabrication stage. The following two experiments were developed to examine this process.

2.2.1 Preexisting Pinholes

The presence of pinholes was tested on both tape and wire. The presence of pinholes was tested by using the knowledge of bubbling in previous conductors. Bubbling was an issue for processing long lengths of Bi-2212 tape\(^{13}\). Gas that had been trapped inside the wire during the heat treatment expanded and cause outward bubbling of the sheath\(^{22}\) as seen in Figure 2.7. This phenomenon would be used to detect if pinholes were present in the current wire. If the samples had pinholes, dipping them into a cryogen would allow the flow of liquid inside the wire. By bringing the samples to high temperature quickly, the liquid would vaporize and expand rapidly and cause bubbling in the samples. In order to evaluate this behavior, Bi-2212 tape and wire was used.
One meter of Bi-2212 tape was used in each of these tests. For information about batch number, see Section 2.1.1. An unreacted batch of tape ppm 021212-2 and a reacted batch of tape ppm 011127-2 were used. Three different wire samples were used in this test; “as received”, drawn though 1 die, and drawn through 3 dies. The wire samples were from the same batch and were green wire. The diameter of “as received” wire was 1.08 mm, the first draw brought the diameter down to 1.06mm, and three draws brought the samples down to 1.00 mm. The drawing process was done to exacerbate any preexisting holes in the wire, causing them to become larger with each consecutive draw. The ends of Bi-2212 tape and wire were sealed with Stycast epoxy and after the first test, the Stycast end were cut off. The samples were then wrapped onto a coil former of G-10 roughly 6 mm in diameter using kapton tape to hold it firmly. The samples were lowered into a bath of cryogen for 5 minutes. Liquid helium and liquid nitrogen were both used as cryogen in separate tests. The samples were then removed from the cryogen and immediately warmed with a heat gun. The samples were visually inspected for any signs of expansion of Ag on the surface of the wire.

2.2.2 Other Surface Defects

In order to look for the source of leakage, a fully reacted coil that leaked was deconstructed and its surface was investigated using optical microscopy for any noticeable
defects within the region that had leaked. The coil used was TC 2007-013 made from batch number pmm 050831 and had a sol gel insulation coating made of Zirconium Oxide rather than the usual alumino silicate braid insulation. The advantage of this coil was that the ZrO$_2$ insulation coating changed color in the regions where leakage had taken place. Several turns from the half coil were examined optically and using optical microscopy. In regions that had leaked, cracks running along the length of the wire were found. Figure 2.8 shows images that were taken of longitudinal cracks found on the surface of the wire.

![Figure 2.8: Wire from TC 2007-013. Longitudinal defects can be seen in leakage regions and are circled in red.](image)

After becoming familiar with the defects that caused leakage in the wire, the surface of the green round wire was examined to see if these types of defects were present in the green wire from the same batch of wire that the coil was made from, pmm 050831, and a new batch of wire, pmm 070601-1. By documenting the defect on the green wire’s surface before the heat treatment, the effect of that defect could be examined after heat treatment to see if they correlated to leaked regions. One meter of conductor was cut into 7 cm long sections and the ends were mechanically sealed. The samples were visually inspected under an optical microscope and digital images were collected of regions having any unusual characteristics included discolorations and longitudinal scratches. The samples were then coated with a
slurry of yttria and butoxyethanol. Yttria does not react chemically with any of the constituents of the conductor but it does wick liquid out from the melt through capillary action.\textsuperscript{23} The samples were then put through the standard heat treatment in an oxygen atmosphere. After the heat treatment, the samples were investigated visually, both with the yttria and with yttria scraped off the surface lightly. The sections that appeared to have leaked were examined under scanning electron microscope (SEM) and leaks were evaluated using energy dispersive spectroscopy (EDS) for elemental analysis.

2.3 Effects of Insulation

Insulation is known to stick to the surface of the conductor, but little work has been done to look at the impact of the braid insulation on the wire itself. Therefore, the impact was investigated in the following ways, by viewing the reactions the insulation has on pure Ag and effect the insulation has on $I_c$.

2.3.1 Reactions Between Insulation and Ag

Several types of Al$_2$O$_3$, amorphous SiO$_2$, and alumino silicate insulation were tested to investigate if they reacted with Ag. The samples included a series of 3M NEXTEL fibers, (Table 2.2) with varying compositions of Al$_2$O$_3$, amorphous SiO$_2$, and B$_2$O$_3$, as well as pure SiO$_2$ fibers. The experiment was done by placing fibers in direct contact with Ag. In order to provide that contact, samples were placed inside sleeves of Ag that were made by rolling a small pure silver rectangular billet. After a few passes through the press, the Ag was annealed using a hot plate. The pure Ag was rolled until it was 100 $\mu$m thick.
Figure 2.9 describes the sample preparation process to place the fibers in Ag pockets. Rectangles approximately 2.5 cm by 3 cm were cut from Ag foil (a). The Ag foil rectangles were folded so that the bottom edge of the 3 cm side now was touching the middle line of the foil. The sample fibers were woven into a fabric, so a single bundle of fibers was removed from the fabric for the tests. With the silver foil rectangle on a table, the fiber bundle was placed along the longest distance in the channel created by the fold (b). The Ag foil was pressed lightly together (c) then folded over once more (d), leaving a region of foil not folded into the rest that would later be used to identify the fiber within the sample. Any overhanging fibers were trimmed to be flush with the edges of the Ag (e). The pockets were annealed at 820°C in a pure O$_2$ atmosphere for 4 hours to burn out any organic materials. The samples were removed, pressed carefully together with a pair of flat jaw pliers, and the ends were crimped together by squeezing shut with flat jaw pliers (f). The samples were then subjected to a standard heat treatment in flowing O$_2$. 

### Table 2.2: 3M NEXTEL fibers. Each fiber was tested for its reaction with Ag.

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>NEXTEL 312</th>
<th>NEXTEL 440</th>
<th>NEXTEL 550</th>
<th>NEXTEL 610</th>
<th>NEXTEL 720</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filament Diameter</td>
<td>μm</td>
<td>10 to 12</td>
<td>10 to 12</td>
<td>10 to 12</td>
<td>10 to 12</td>
<td>10 to 12</td>
</tr>
<tr>
<td>Crystal Size</td>
<td>nm</td>
<td>&lt;500</td>
<td>&lt;500</td>
<td>&lt;500</td>
<td>&lt;500</td>
<td>&lt;500</td>
</tr>
<tr>
<td>Crystal Type</td>
<td></td>
<td>9Al$_2$O$_3$·2B$_2$O$_3$ + amorp. SiO$_2$</td>
<td>gamma Al$_2$O$_3$ + mullite + amorph SiO$_2$</td>
<td>gamma/delta Al$_2$O$_3$ + amorph SiO$_2$</td>
<td>alpha Al$_2$O$_3$</td>
<td>alpha Al$_2$O$_3$ + mullite</td>
</tr>
<tr>
<td>Filament Tensile Strength</td>
<td>MPa</td>
<td>1700</td>
<td>2000</td>
<td>2000</td>
<td>2930</td>
<td>2100</td>
</tr>
<tr>
<td>Filament Tensile Modulus</td>
<td>GPa</td>
<td>150</td>
<td>190</td>
<td>193</td>
<td>373</td>
<td>260</td>
</tr>
<tr>
<td>Composition</td>
<td>wt%</td>
<td>62 Al$_2$O$_3$, 24 SiO$_2$, 14 B$_2$O$_3$</td>
<td>70 Al$_2$O$_3$, 28 SiO$_2$, 2 B$_2$O$_3$</td>
<td>73 Al$_2$O$_3$, 27 SiO$_2$</td>
<td>&gt;99 Al$_2$O$_3$, 0.2-0.3 SiO$_2$, 0.4-0.7 FeO$_3$</td>
<td>85 Al$_2$O$_3$, 15 SiO$_2$</td>
</tr>
<tr>
<td>Reaction with Ag</td>
<td></td>
<td>Complete Ag penetration in fiber and surrounding matrix material</td>
<td>Complete Ag penetration in fibers with increasing radial content</td>
<td>Reaction layer in fibers, center of bundle unreacted</td>
<td>No reaction</td>
<td>No reaction</td>
</tr>
</tbody>
</table>
When the heat treatment had ended, the samples were removed. The Ag had large visible grain boundaries that could be seen by the naked eye. The samples were prepared to be viewed in the SEM using the standard microscopy preparation (See Section 2.1.7) with a few variations that are described below. Figure 2.10 is a diagram of the sample prep done to the puck. A puck, which is a cylinder, is oriented as shown in (a). The curved surface was sanded flat in three locations (b) and several slits are cut into the flat using an Isomet 4000 low-speed saw.

**Figure 2.9:** Diagram showing how to prepare samples to test for reactions between fiber and Ag.

**Figure 2.10:** Diagram for microscopy preparation. The carbon pucks were prepared by grinding in the sides and cutting slits to accommodate the insulation samples.
A total of three flats were sanded into the puck and several slits are cut into each flat. The Ag samples were cut in half perpendicular to the direction of the fibers. Half of the Ag sample was placed into the slits of the puck in a specific orientation. The puck, with samples (c), was placed back into the Simplimet Mounting Press with more mounting compound. After the mounting press cycle was complete, the puck was a full cylinder again with the samples locked in the solid mounting compound (d). The grinding procedure was then followed but the Vibromet was not used. In order to compare the samples to the as received state, aluminum foil was used instead of Ag and the samples were not heat treated. The as received fibers were mounted and polished in the same manner as the reacted fibers. The samples were cleaned and then viewed using a Zeiss 1540 EsB Scanning Electron Microscope.

2.3.2 The Effect of Insulation on $I_c$ of the Conductor

The alumino silicate insulation consistently drives down $I_c$ of the insulated samples. The purpose of the insulation-on-conductor experiment was to simulate the effect on samples that would be seen on a coil former but to minimize the other variables that could have an effect on performance. Achieving good contact between the insulation and the surface was a major problem. When cut, the braid would unravel leaving a section close to the cut completely uncovered and the unraveled section would become larger with any manipulation. When wound in a coil, the insulation is pulled tight on the surface of the conductor from the winding process and the other turns hold it in place. Insulation on short samples is not kept taut along the entire length of the wire. When the insulation is in close contact with the surface of the wire, regions of braid stick to the surface forming a tire track pattern. Maintaining good surface contact and have discrete sections of insulation needed to be overcome before a successful experiment could be executed.

The first samples were made into small diameter spirals. The samples were wound in a tight diameter to provide the tension in the braid. The spirals were four turns around a diameter of 8 mm. A spiral with insulation and a sample that was bare were created as a pair. A vertical quench furnace was used for the samples. The vertical furnace has the samples hang in the homogenous zone (See Section 2.1.3 and 2.1.4). The samples were attached to
sample mounts at two points using insulation and hung in the homogeneous zones. A single spiral was attached to a single sample mount and was placed down one of the four sample tubes that exist within the quench furnace. After a standard heat treatment in an oxygen atmosphere, the samples were inspected. These samples did not exhibit sticking of insulation on the Ag surface, meaning that this configuration was not able to reproduce the conditions necessary for this study. Since the curvature was not keeping the insulation taut on the wire, the spiral configuration was abandoned.

![Diagram of samples]

**Figure 2.11:** Side-by-side samples. Left is a schematic and right is the actual samples. The top is insulated and has the Ag wire warp holding the insulation on the surface of the wire. The bottom is bare wire.

A second set of samples was used in order to achieve the needed conditions. A small diameter pure Ag wire was wrapped around the outside of the insulation, keeping the insulation in place and maintaining the interface between conductor and braid, as seen in Figure 2.11. A pair of samples, one insulated and wrapped with Ag wire and the other bare conductor, were attached to the quench furnace sample mount. These side-by-side samples would subject the two samples to identical heat treatments. The Ag wire was drawn to 0.8 mm diameter in-house. Ag was selected for the wrap since it added no new chemical elements to the system and due to the ability of $O_2$ to diffuse through it quickly. This Ag was wrapped before the wire was cut so that the insulation would not fray for the insulated samples. The wire was then cut to the length of 3 cm. The ends of the samples were closed by hammering shut with a punch. These wire samples were attached to a sample mount using insulation. This sample mount had two loops to allow two samples to be heat treated in a single sample
tube. The proximity between the insulated and bare sample ensured that both samples would see the same heat treatment. One set of samples was placed in the quench furnace for a standard heat treatment in an oxygen atmosphere and they are referred to as the side-by-side samples. Another set of samples was quenched at temperatures surrounding the formation of Bi-2212 on cooling; 872, 870, 868, and 866°C.

A second test was used to evaluate the effect of the insulation across the same sample. A 12 cm length of conductor was used for this test, referred to here as the striped samples. It is shown in Figure 2.12.

![Figure 2.12: Schematic and image of striped sample. Each section is 3 cm in length for a total of 12 cm long.](image)

The first 3 cm were insulated and wrapped with Ag wire in order to achieve the tight contact of braid and Ag. The following 3 cm had the insulation removed so that it was bare. This alternated down the sample to have 4 distinct sections measuring 3 cm each, creating a striped sample. Sections A and C were braided while sections B and D were bare. Two
samples were made so that the samples could be investigated in multiple ways. The samples were heat treated in the Lindberg Blue furnace using a standard heat treatment in an O₂ atmosphere. After heat treatment, the samples were cut at the interface between the insulated and bare wire.

The side-by-side and striped samples had the Ag wire removed in order to evaluate the samples. The surface of the Ag that was in contact with the insulation had the tire track pattern on the surface. The side by side samples were 3 cm long and in order to measure Iₐ a length of 4 cm is needed, so superconducting tape was used to bridge the samples (Figure 2.6) in order to take the measurement.

The electromagnetic tests were done on small lengths of wire cut from the second striped sample. A 0.34 cm section was cut from the center of these new segments A through D. The samples were tested using an Oxford 14 T Vibrating Sample Magnetometer (VSM) and a Quantum Design: MPMS-XL5s SQUID in the Applied Superconductivity Center. In the VSM, the samples were run at both 5 K and at 20 K with field perpendicular and parallel to the wire. The VSM measures magnetic moment. In the SQUID, the sample’s remnant field was measured when the field was applied parallel to the wire axis. The magnetic moment was also measured in the SQUID at 10 Oe.

The side-by-side and quench samples were mounted and polished using the standard procedure for SEM and evaluated using EDS.
CHAPTER 3
RESULTS

3.1 Leakage

3.1.1 Preexisting Pinholes

One of the first hypotheses for leakage was that pinholes existed in the green wire. After the samples were submerged in cryogen (LN₂ and LHe) and heated quickly to cause any cryogen in the wire to expand, there were no signs of bubbling or any expansion of any type in either the tape or the wire. The wire samples were drawn to a smaller size in order to exacerbate any holes that might exist, but still no bubbling was seen. Even after the Stycast ends had been removed, the samples still did not show signs of bubbling.

3.1.2 Surface Defects

![Sample Images](image)

**Figure 3.1:** Samples with yttria after the heat treatment. Six out of the six samples show signs of leakage, which can be seen as regions of discoloration in the images.
The surface of the green wire was examined. Any irregularity across the surface was recorded. In the heat treatment of batch number pmm 050831 (old generation), 6 out of the 16 total samples were selected because they had defects that were thought possibly to cause leakage. Out of the 6, all showed at least a single sign of leakage across the 7 cm cross section, seen in Figure 3.1.

The yttria was scrapped off to view the wire’s surface optically and under the SEM. Similarities between the green irregularities and the leakage locations were noted. Figure 3.2, shows a wire where a crack was identified in the green wire and that same region had leaked in the leak test. Longitudinal cracks of a similar size and depth were seen along the length of the conductor several times, but did not always result in leakage. Figure 3.2 shows another region with leaked material. This sample was investigated using EDS to see the composition, which showed all four constituents of BSCCO to be present. The large amount of leaked material coating the surface of the conductor could not be removed, so the surface defects in the Ag that caused leakage could not be noted.

![Figure 3.2: (a) Green Wire showing long defect (b) Same region of wire shown in (a) after the heat treatment. Yttria can be seen in the image as white particles on surface.](image)

Samples of wire with a batch number pmm 070601-1 (new generation) were examined using the same procedure as the previous wire. Again, 6 samples were selected. After heat treatment, no evidence of leakage was found on any of these samples. Therefore, the leakage investigation was discontinued.
3.2 Insulation

The insulation provides a thermal barrier between turns of the conductor at high temperatures during the heat treatment. The insulation used currently is 73/27 wt% Al$_2$O$_3$-SiO$_2$ (mullite composition) consisting of crystalline Al$_2$O$_3$ and amorphous SiO$_2$. The insulation is braided around the conductor in the green state. J. Jiang’s images of insulation sticking into the surface of the wire$^{17}$ motivated this work that focused at looking at the effect of the insulation on the conductor.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrL</td>
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<td>25.75</td>
</tr>
<tr>
<td>BiM</td>
<td>48.91</td>
<td>26.20</td>
</tr>
<tr>
<td>AgL</td>
<td>00.00</td>
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<tr>
<td>CaK</td>
<td>02.62</td>
<td>07.31</td>
</tr>
<tr>
<td>CuK</td>
<td>10.13</td>
<td>17.84</td>
</tr>
<tr>
<td>YK</td>
<td>18.19</td>
<td>22.91</td>
</tr>
<tr>
<td>Matrix</td>
<td>Correction</td>
<td>ZAF</td>
</tr>
</tbody>
</table>

Figure 3.3: Evaluating a leak. (a) Sample with yttria coating and discolored region (b) Sample after removal of yttria (c) SEM image of leakage section (d) EDS of region showing all four constituents of Bi-2212
3.2.1 Reactions Between Insulation and Ag

The results of NEXTEL 312, 62 wt% SiO$_2$, 24 wt% Al$_2$O$_3$, 14 wt% B$_2$O$_3$ amorphous in contact with Ag are shown in Figure 3.4. When exposed to Ag, the individual fibers created one large composite of material. Ag was present in the entire cross section but in varying amounts. All of the weight percentages given below are calculated only considering Al, Si, and Ag. B was not detected and so its weight percentage was not included and may have an effect on the results. Two distinct phases are present. The first phase is what looks like the individual fibers colored black. Using point analysis with the EDS, these regions contained 27-35 wt% Ag through the oval cross section. The second phase is light grey and is the material in-between the fibers. This region has an Ag content of roughly 58 wt% Ag. This secondary light grey material has encased the first and created a composite. The material fractures as a unit and not as individual fibers. This material has become glassy and brittle.
Figure 3.5: NEXTEL 440 fibers after reaction. Ag has penetrated completely into sample but fibers still remain discrete.

NEXTEL 440 is similar to NEXTEL 312 but with a smaller $B_2O_3$ content, with a total composition of 70 wt% $SiO_2$, 28 wt% $Al_2O_3$, 2 wt% $B_2O_3$ amorphous. These fibers did not merge into one large matrix but did have a Ag content throughout as can be seen in Figure 3.5. Even the center of the fiber, which is displayed in black on the image, has a Ag content reaching 5 wt%. The edge of the filament reach as high as 50 wt% Ag.

Figure 3.6: NEXTEL 550 fibers after reaction. Distinct reaction layer of Ag in fibers is shown. This composition is the same as insulation used on the wire.

NEXTEL 550 has a composition of 73/27 wt% $Al_2O_3$-$SiO_2$ (mullite composition) consisting of crystalline $Al_2O_3$ and amorphous $SiO_2$. This fiber has the same composition as the fiber used to insulate the superconductor. After the reaction Figure 3.6, the 550 fibers visually seem to be separate individual fibers with a region of Ag penetration. The center of the fiber (black region) contains less than 2 wt% Ag. This amount could be attributed to
background measurements. The region of Ag penetration (light grey) measures from 30-35 wt% Ag. At the largest section, the fiber bundle is five fibers thick. In this section, all the fibers have Ag penetration.

**Figure 3.7:** NEXTEL 720 fiber after reaction. The Ag reaction layer was not observed within the sample shown.

NEXTEL 720 has a composition of 85/15 wt% Al$_2$O$_3$-SiO$_2$ – crystalline Al2O3 + crystalline mullite (3Al$_2$O$_3$-2SiO$_2$). The 720 fibers are more brittle than 312, 440, and 550. The fibers showed no reaction layer with Ag, as seen in Figure 3.7.

**Figure 3.8:** NEXTEL 610 fibers after reaction. The Ag reaction layer was not observed within the sample shown.
NEXTEL 610 has a composition of >99% Al₂O₃. The 610 fibers were the most brittle of all the fibers, having no amorphous SiO₂. These fibers also showed no reaction with Ag, which can be seen in Figure 3.8.

![Image of Pure SiO₂ fibers after reaction.](image)

**Figure 3.9:** Pure SiO₂ fibers after reaction. Samples received the heat treatment twice. The Ag reaction layer was not observed within the sample shown.

One additional sample was tested in addition to the of NEXTEL fibers. This was a high purity silica material made of >97wt% SiO₂. The fibers were very soft and ductile. They were easily crushed when being closed in the Ag pocket. A very small or no reaction layer was seen in this sample, seen in Figure 3.9.

3.2.2 The Effect of Insulation on Iₐ of the Conductor

3.2.2.1 Transport Current Data

![Image of Bare and Insulated wire surface.](image)

**Figure 3.10:** Wire surface of striped samples after heat treatment. Insulation can be seen sticking to the surface

After the heat treatment, the Ag wire that had surrounded any braided samples was very soft after the full heat treatment and needed little effort to be removed. The insulation
flaked off the sample and the sticking braid was seen on the surface in Figure 3.10, which indicates the success of the experimental setup in having good contact between the insulation and the surface of the wire. The samples were then attached to MSP3 and measured at 4.2 K and 5 T. $I_c$ data for the side-by-side samples are shown in (Figure 3.11). The insulated sample of pair 3 was damaged during testing and no data was obtained from the sample. The $I_c$ in the insulated samples was 20-25% lower then their bare counterpart samples.

![Side-by-Side Ic Data](image)

**Figure 3.11:** $I_c$ of side-by-side samples. The insulated sample of pair number 3 was damaged during measuring and was not readable. The insulated samples performance is roughly 20% lower than the bare samples.

$I_c$ data for the striped samples are shown in Figure 3.12. The insulated segments perform roughly 20% less than bare regions.
3.2.2.2 Electromagnetic Properties

For the next set of data, the naming convention has been changed for ease of understanding of the reader. The samples have been labeled Insulated 1, Insulated 2, Bare 1, and Bare 2. The state of the sample, insulated or bare, is indicated in the naming convention. Samples with the number 1 indicate end sections, meaning Insulated 1 corresponds to section A and Bare 1 corresponds section D. Samples with the number 2 indicate middle sections, meaning Insulated 2 corresponds to section C and Bare 2 corresponds to section B. With this naming convention comparison can be made easily between similar samples.
The Kramer data is calculated from magnetic data at 20 K with field perpendicular to the wire. The Kramer plot is a measure of the Kramer irreversibility field and can be seen in Figure 3.13. The plot contains data on all four samples. The lines of three samples overlap. Insulated 2 is the only sample that does not have the exact same plot. Each curve has a linear regime located after the peak. The Kramer field is determined by extending the linear regime down to the x-axis, which gave $H_k$ as 7.6 T. Although Insulated 2 does not have the same peak value, the magnitude of the slope of the linear regime is larger which results in an equal Kramer value.
Table 3.1: Change in magnetic moment measure at 5T from the VSM. Left column is the measured value and the right column is normalized to mass.

<table>
<thead>
<tr>
<th>Sample</th>
<th>dMoment (emu)</th>
<th>dMoment/mass (emu/mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insulated 1</td>
<td>8.26E-02</td>
<td>3.56E-03</td>
</tr>
<tr>
<td>Insulated 2</td>
<td>7.33E-02</td>
<td>3.14E-03</td>
</tr>
<tr>
<td>Bare 1</td>
<td>8.20E-02</td>
<td>3.52E-03</td>
</tr>
<tr>
<td>Bare 2</td>
<td>7.91E-02</td>
<td>3.42E-03</td>
</tr>
</tbody>
</table>

The magnetic moment was measured at 4.2 K with the field perpendicular to the wire and the values can be seen in Table 3.1. The samples were brought up to 14 T and then ramped down at 4.2 K and with the magnetic field perpendicular to the wire axis. The change in magnetic moment was compared at 5 T when the applied field was being ramped down. The value was divided by the mass to normalize the values for comparison. The magnetizations were very similar and the largest difference was within ±8% of the average.
Figure 3.14: Magnetic moment measurements of striped samples at different temperatures. The bare samples measured better than the insulated samples.

$T_c$ measurements were done on the sample using the SQUID. Two separate $T_c$ plots are shown. The first (Figure 3.14) is the $T_c$ measurements normalized to the mass of the sample. The second plot (Figure 3.15) is data for the samples normalized to their value at 5 K for comparison. The plots show all the samples $T_c$ at the same value of roughly 82 K. In Figure 3.14, Bare 1 and Bare 2 have consistent values that are below that of Insulated 1 and Insulated 2. Figure 3.15 has a bit of separation in between 40-60 K, with two distinct bands for the bare and insulated samples with the insulated samples above the bare samples.
Figure 3.15: $T_c$ plot of striped samples. The separation at temperatures 40-60 K is distinct between bare and insulated samples.

The remnant field contains information about the connectivity of the sample. The first curve is of remnant field as a function of applied field (Figure 3.16). The samples all saturate at the same applied field but have different plateau values. Bare 1 and Bare 2 have a similar slope and separation from the two insulated samples until Bare 1 saturates.
Figure 3.16: Remnant field data at 5 K and with the applied field parallel to the wire axis. All samples saturate at the same applied field but the insulated samples have lower values.

After taking the derivative of the remnant field data in Figure 3.16, a second curve is obtained, which is shown in Figure 3.17. The Ic data is included in the legend of Figure 3.17 for quick reference. Two peaks are seen on this plot. The first peak (at low field) relates to the global current, the current flow across grain boundaries as it completes long range circulation. The second peak (at high field) relates to local current, or the current flowing intragrain as it completes short range circulation. The first peak corresponds to the breakdown of the axial current which is related to the Ic of the sample. Insulated 1 performed the worst in both Ic and in the first peak of the remnant field. Bare 1 and 2 had similar values for both the Ic and the remnant field. Insulated 2 shows an 18% reduction compared to the bare samples while Insulated 1 shows a 25% reduction. The height of the first peak and the Ic data agree, having the highest Ic performing sample be the one with the highest first peak. The second peak has more of a scatter in the data but the highest performing sample is a bare one.
Figure 3.17: Derivative of Remnant Field data at 5 K and with field applied parallel to wire axis. First peak shows intergrain current while second peak shows intragrain current. Insulated samples perform worse in the first peak which corresponds to the $I_c$ values shown.

3.2.2.3 Microstructure Analysis

The cross section of the insulation that is stuck on the surface of the wire is shown in Figure 3.18. Each fiber contains a core with $Al_2O_3$ and $SiO_2$ with a reaction layer that contains $Al_2O_3$, $SiO_2$, Ag, and small amounts of Cu. Several points, labeled on in Figure 3.18 (a) with letters, were examined for their content. The composition of Cu and Ag in weight percent is given in Figure 3.18 (b). The Cu content is highest at the interface between Ag and the insulation and decreases quickly across the cross section of the fiber. The spectrum of point A and point E are shown in the image. Figure 3.18 (c) shows that the K and L Cu peaks can be seen at point A. Figure 3.18 (d) shows the Cu peaks for point E are very small compared to the peaks at A.
Figure 3.18: SEM and EDS of insulation on striped samples. (a) SEM image with points label where EDS analysis was conducted. The reaction layer can be seen in the fibers. (b) Table with values of Cu content and Ag content at the regions labeled in (a). (c) Spectrum from position A. Cu peaks can be seen both in the L and K shell. (d) Spectrum from position E. Cu peaks are very weak.

The quench samples had unexpected microstructure which prevented the phase evolution from being examined in the capacity that was intended. When viewed under an optical microscope, large regions of the center bundle were missing. The pores were initially thought to be caused during grinding and polishing by breaking parts of the filaments away and exposing a large hole where the filaments would normally reside. The samples were ground and polished again but the porosity persisted. The images taken at the last stage of grinding do give some clues that this porosity is not the caused by user error during the grinding process.
Figure 3.19: Quench samples with massive porosity. Images (a) and (b) are quench samples while samples (c) and (d) are green wire. Images (a) and (c) from batch number pm070414-4 and images (b) and (d) are from batch number pm070420-4.

The second grind was done with extreme care. Green wire of these two batches was also examined to determine if any features could lead to the results of the quench studies. Two issues seem to affect the cross section of the wire. First, parts of the central bundle are completely missing and instead show up as regions with large porosity. This is evident in Figure 3.19 (a), where the middle bundle appears as a black region. The size of the filaments around the region of porosity is highly non uniform. The image shown is not a polished sample and therefore has no loose Ag removed from it. Very little liquid seems to be occupying any space around the pore. This can also be seen in Figure 3.19 (b) but in this case, the filaments within the Ag matrix are gone.
A secondary issue can be noted along the interface between the filament bundles and the Ag-Mg sheath. In all generations of wire, small voids exist where complete bonding has not taken place between the Ag and Ag-Mg sheath. In wire’s with batch numbers pmm 07-0414-4 and pmm 070420-4, large voids exist and seem to affect the filaments in close proximity to the void. In Figure 3.20 (a), the bottom filament shows a large pore where the interface would normally reside. The other sample Figure 3.20 (b) has a result that seems similar but is not as severe, but this pore region is filled in with the Ag.

Figure 3.20: Quench samples with Ag and Ag-Mg interface issues. (a) Sample quenched at 870°C has interface issue in bottom filament. Filaments are pushed inwards. (b) Samples quenched at 872°C with interface issue at left bundle. Filaments again pushed inward.
CHAPTER 4

DISCUSSION

4.1 Leakage

4.1.1 Preexisting Pinholes

Dip testing in cryogen the samples provided no visual evidence of bubbling from tapes and wires, reacted and unreacted, ends sealed and open. Two conflicting conclusions can be drawn from this. The first is that there are no pinholes in the wire. The second conclusion is there are pinholes, but the sample is unable to exhibit the expected response. If the liquid resides within the wire, does the amount of liquid have the force to expand the silver-magnesium sheath material? The bubbling seen in the tape in Figure 2.7 was done at high temperature. H$_2$O bubbling occurred at 700°C, while C and O bubbling occur around the melting temperature of Bi-2212 which can be between 850-870°C$^{22}$. Gasses released from the powder pushed against the inside of the sheath when the entire system is around the partial melt temperature. The strength of the material at high temperature is much lower than the cryogenic case. There is also no way of measuring the amount of liquid entering the conductor. These variables cast a shadow on this experimental method of testing for pinholes. Another method of proving pinholes exist would need to be used to verify this result.

4.1.2 Other Surface Defects

The 6 yttria coated samples of old generation conductor batch pmm 050831 (Figure 3.1) all showed signs of leakage after the heat treatment. These leakage points correlated to long longitudinal cracks on the surface of green conductor (Figure 3.2). Visual inspection of the green wire suggests that these cracks did not completely penetrate into the filaments of the conductor, but the sheath is thinner below the crack. During the heat treatment, the liquid dissolved Ag until its content in the liquid is roughly 5 wt%$^{25}$. The crack may have a thin enough cross section for the Ag to completely dissolve away and allow Ag rich liquid to
escape. Thus, the longitudinal cracks can have no leakage or leakage only in localized regions within the crack. When there was severe leakage, a thick layer of yttria and BSCCO found on the surface of the conductor prevented the correlation between the surface defects in green and heat treated wire to be made due to the inability to see the Ag surface.

Due to the correlation of the leaks to the cracks, the preliminary conclusion was that a manufacturing process was the cause of the cracks and thus, the leakage. Since the wire used is from Oxford Superconductor Technology, a meeting was scheduled with them to discuss the preliminary findings. At that meeting, OST said that we were investigating “old” generation wire that leaked and that they were now manufacturing “new” wire that did not leak. OST had internally mitigated or significantly decreased the problem of leakage. This led to the classification of old generation wire that leaked and new generation wire that OST said did not leak. Since leakage was solved by OST, the study moved to investigating reactions with insulation.

**Figure 4.1:** Old generation and new Generation wire. (a) Cross section of old generation wire with inset of wire surface (b) Cross section of new generation with inset of wire surface

Old generation (OG) wire has a pitted surface that is dull when looked at with the naked eye, seen in the inset of Figure 4.1 (a). When looking at the cross section, the OG wire’s surface has mushroom shaped formations extruding from it and defects run longitudinally along the length of the wire (Figure 3.2 (a)). The OG wire is brittle as received which suggests the wire received a long, high temperature anneal. The pitting on the surface is characteristic
of Ag loss and the surface formations are where the MgO particles remain. The Mg in the sheath has reacted with O\textsubscript{2} causing MgO formation, which increases the brittleness of the wire. A final draw may have taken place after the long, high temperature heat treatment in order to densify the powder further.

The new generation (NG) wire has a smooth, almost mirror-like surface with few defects (Figure 4.1 b). The surface defects found on the NG wire are an order of magnitude smaller (inset of Figure 4.1 (b)) and do not cause leakage. It seems that NG wire has not been heat treated like the OG wire. When coated with yttria and heat treated, the new wire samples did not leak.

Defects in the wire may not be the only cause of leakage. J. Jiang showed that the insulation wrapped around the conductor was reacting with the Ag\textsuperscript{17}. The insulation can be seen sticking to the surface of the conductor in a repeating tire track pattern and its contact with the surface may be the driving force for the leaked material to come out.

4.2 Effects of Insulation

4.2.1 Reactions Between Insulation and Ag

The 3M NEXTEL fiber results were presented in order from highest amorphous silica content to no amorphous silica content. The greater content of silica in the sample creates more flexible fibers, as can be seen by the decreasing tensile modulus in Table 2.2. Another trend can be seen that the greater the amount of amorphous silica, the more severe of a reaction layer with Ag, which can be seen in Table 2.2. Seeing that the conductor sheath is primarily Ag, many of the potential insulation materials tested are highly reactive with a major component of the wire. From a reaction standpoint, the best insulation material is one with a high alumina content, but the high purity alumina fibers can be difficult or even impossible to braid due to their stiffness. The 73/27 wt\% Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} composition used currently on the conductor had the smallest reaction layer and lowest Ag content measured in the braid, but the fiber is taking Ag away from the surface and is thought to help cause leakage. In Figure 3.6 the fibers are surrounded by Ag up to 5 \textmu m into each side. The thickness of the sheath in the Bi-2212 wire is ~50 \textmu m, which is 10 times thicker. Therefore, the insulation is not the cause of
leakage but can exacerbate it in two ways. First, it removes Ag from the surface. Second, the sticking insulation acts like the yttria on the surface of the wire, helping to wick out liquid in the partial melt phase where cracks exist. The fibers were reacted with pure Ag, which means other interactions between other constituents in the wire could take place.

The high purity SiO$_2$ fiber did form a singular matrix or have a reaction layer like the NEXTEL fibers with higher silica. There was no reaction with Ag. This fiber has great flexibility and is very thin and seems the perfect candidate for insulation; however, in the presence of salts, amorphous SiO$_2$ incorporates the salt and becomes a lower temperature melting glass. To investigate how this high purity SiO$_2$ fiber would react in the presence of salts that could be incorporated during winding, the same reaction done with SiO$_2$ was repeated, but small amounts of NaCl and KCl were added to represent contamination from sweat or other salts that can be on the surface of a hand or picked up in a manufacturing facility. The result was a complete loss of individual filaments when the heat treatment was done with NaCl and KCl. Instead, they form massive blocks of SiO$_2$ and salt plus Ag, as seen in Figure 4.2. A severe reaction at a single part of the braid is unwanted, so we do not recommend using pure SiO$_2$ as an insulation material.

Figure 4.2: Pure SiO$_2$ fibers reacted with KCl and NaCl (a) SiO$_2$ reacted with KCl. Fibers fuse together and become one large mass. (b) SiO$_2$ reacted with NaCl. Fibers again form a single unit.
4.2.2 The Effect of Insulation on $I_c$ of the Conductor

The side-by-side and striped sample configurations both resulted in a reduction in $I_c$ of 20-25%, as seen in Figure 3.11 and Figure 3.12. The side-by-side samples discount any criticism about the inhomogeneity of the heat treatment because the samples occupied were only a few millimeters away from one another during the heat treatment. The striped sample results show that the insulation is not affecting the ends of the sample in any way because the $I_c$ loss is the same in the middle regions. This data also is consistent with the long witness samples where the $I_c$ is higher in the bare wire shown in Figure 1.7.

The mechanism causing the $I_c$ loss with the sheath is not obvious. The samples all have very similar Kramer field values. The Kramer irreversibility field evaluates the flux pinning in the individual grains of the sample. By viewing the Kramer plot, the quality of the Bi-2212 grains in the wire is evaluated. More specifically, by circulating current in a single grain, the grain’s ability to pin flux may be determined. With the Kramer field a measure of current circulating in grain, the samples (Figure 3.13) exhibit similar flux pinning in their superconducting grains. Insulation does not seem to have an effect on the pinning in the Bi-2212 grains.

The magnetic moment is a measure of the magnetic field around the conductor. This includes a sum of all the local and global circulating currents in a sample. The variation in the magnetic moment data (Table 3.1) is ±8% of the average with no noticeable trend between bare and insulated wire, so the samples still look similar.

The $T_c$ trace (Figure 3.14 and Figure 3.15) determines the superconducting transition of the samples. This transition is dependent on two aspects; the oxygen uptake of the sample and the amount of defects within the sample. The oxygen content of the conductor relates to the actual temperature that the samples become normal. The defects in the sample affect the temperature range at which the samples start to become normal. If the transition region has a higher $\Delta T$ the sample has more defects. The consistent $T_c$ values (Figure 3.14 and Figure 3.15) show that the samples globally have the same oxygen content. The uniformity in the sample’s oxygen content is the only firm result that can be determined from these plots, but the shape of the curves allows for some speculation as to the mechanism for $I_c$ loss. Figure 3.14 shows Bare 1 and Bare 2 have the most shielding. By averaging the value of Bare 1 and Bare
2 at 5 K, the difference between the average and the values for samples Insulated 1 and 2 can be determined. Insulated 2 has only a 3% difference from the bare average while Insulated 1 has an 8% difference. This indicates the possibility of less superconducting phase in the insulated wire, specifically when looking at the low temperature region. Figure 3.15 shows samples that are located on the ends, Insulated 2 and Bare 2, both have lower curves than the middle sections indicating a sharper transition. In the 40-60 K temperature range, the bare end sample has about 10% more negative normalized magnetization compared to the end insulated sample. The same 10% more negative magnetization is seen when comparing the bare middle section to the insulated middle section. This difference between bare and insulated sections indicates a decrease in connectivity of the insulated samples compared to the bare samples. Insufficient grain growth would explain an issue in connectivity and is a possible conclusion from these results.

The remnant field data shows the difference in the first peak (Figure 3.17), which is due to intergrain current. The insulated sample’s lower values for the first peak than for the bare samples indicate that the insulated samples have a reduced ability to have current flow across grain boundaries. Therefore, the $I_c$ of the samples with the lower first peaks was limited due to a decrease in connectivity between grains. The insulated samples have either changed the alignment of the Bi-2212 grains, which is unlikely, or changed their growth conditions resulting in fewer grains to carry current.

The current insulation fibers have shown small concentrations of Cu close to the interface with the wire and a decreasing Cu content as the distance from the surface increases (Figure 3.18). The only source of the Cu is from the BSCCO filaments. Cu is soluble in Ag and rapidly diffuses in Ag. Solid state diffusion is the mechanism by which the Cu is able to travel to the braid but only when the wire is in the partial melt. This new finding shows that Cu from the BSCCO core reacts with the $\text{Al}_2\text{O}_3$-$\text{SiO}_2$ fiber. The Cu can be lost from the Bi-2212 core by 3 mechanisms; (1) to Ag (2) to MgO and (3) to $\text{Al}_2\text{O}_3$-$\text{SiO}_2$. If Cu leaves the filaments, the overall composition changes in the BSCCO leading to a greater formation of Cu-Free phases. Also, the Cu loss would lower the overall density of the filaments, leading to more porosity in the system. In the fully heat treated wire, the changed composition could lead to the decreased connectivity and lower $I_c$ in the wire.
Cu loss in the wire seems to be the mechanism that causes losses in $I_c$. Cu diffusion to the insulation would only have an impact on the outer filaments in the outer bundles due to their being closest to the insulation. If the Cu loss affects only the outer two layers of filaments in the outer bundle, 23% of the total filaments in the wire would be affected. The connectivity in these filaments would decrease by the appearance of more secondary phases and pores, causing less aligned Bi-2212 grains and insufficient growth in the wire. The unexpected microstructure of the quench samples prevented the study of the microstructure of quench samples in order to determine if the secondary phase fraction increases in the outer filaments of the outer bundles (Figure 3.19).

4.2.3 Porosity in New Generation Wire

New generation wire helped alleviate the issue of leakage that plagued its predecessor; however, different issues with the wire were discovered. The center bundle has large amounts of porosity in quenched and fully heat treated samples with batch numbers pmm 070413-4 and pmm 070420-4.

Ag can take the place of a void during grinding by the soft metal being pushed into regions that are vacant. T. Shen has investigated the same sample polished by hand and on the Vibromet and found that some regions that are Ag are actually pores in the conductor, having Ag pushed into them through grinding and hand polishing. Using that information on Figure 3.19 (b), the region was porous and is filled in with Ag. (c) and (d) are the green wire of the same batch as (a) and (b) respectively. The green wire has sections in the center bundle filaments that are non uniform and regions that have no Ag between them. In the case of (d), roughly 14 filaments are completely joined together to form one macro filament in the conductor. The non uniformity and the joining bonded filaments seem to be the cause of the porosity. As the conductor enters the peritectic melt, liquid and secondary phases are formed. In the normal architecture of the conductor, the liquid, secondary phases, and pores become distributed across the length of the filament or a pair of filaments because some filament bonding is to be expected. In the case of this conductor, the large macro filaments allow for the congregation of pores and liquid that results in macro pore or macro liquid regions. There has been little evidence of a macro liquid region so the assumption is made that the liquid is
drawn into the individual filament regions into the space where the filaments still remain separate along their length of the wire. The bonded regions then are filled with a congregation of pore material resulting large areas of porosity.

In Figure 3.20, the samples are ground and not polished, and therefore the Ag filling the pore could be from grinding as it is pushed in. The pore has not caused a loss of filaments, but rather a large region that has pushed inward to the center of the bundle and deformed the filaments. The deformation of filaments in these samples cannot occur as a result from the grinding process. The interface regions show signs of expansion inward, causing the deformation of the filaments. A possible cause for this expansion would be organic material that has burned within the wire and exerted a pressure on the interface. The burning of the material would exert a pressure on the interface causing the weaker Ag-filament interface to yield instead of the stronger Ag-Mg interface. This is not consistent with bubbling in the conductor (See Section 2.2.1), but the mechanism causing the deformation is different. In the case of bubbling a buildup of pressure occurs as gas is released from the constituents of the powder. If an organic material were to burn, the pressure change would happen very quickly causing a non-equilibrium stress state. This explanation is purely speculative because no experiments were done in order to try to determine the true cause.

4.3 Final Thoughts

Bi-2212 will have a place in the future only if the limitations of the conductor are overcome. This must first take place on the manufacturing side, through a higher quality control during fabrication of this wire than other conductors. The drive for industry to optimize current density may be less important than to develop a leak free conductor or a conductor with consistent performance along its length and between batches. Dialogue between industry and the research community about known manufacturing issues is required for innovation to happen quickly and concisely.

On the research side, the community must recognize that the conductor is not chemically inert. Many of the materials used in conjunction with the conductor may react with the sheath or the BSCCO constituents. In addition to the previously known reaction between Ag and the alumino silicate fiber, we have shown that Cu also reacts with the alumino silicate
insulation decreasing the Cu content in the Bi-2212 core, which we believe is a key reason $I_c$ is decreased in insulated wire.
CHAPTER 5
CONCLUSION

5.1 Conclusions of Results

5.1.1 Leakage

It appears that leakage has been mitigated by OST changing the wire manufacturing. The insulation may exacerbate the leakage by absorbing Ag causing a thinner sheath material and by wicking the liquid out of defects onto the surface through capillary action. The new wire has shown much less leaking but is still not completely leak-free. As the technology moves towards cabling, the deformation process may again cause a leaky conductor. There may still be some leaks that occur in new generation wire, but there are significantly fewer leaks than in the old generation wire.

5.1.2 Insulation

The alumino silicate insulation used is highly reactive with the conductor. By reacting with both Ag and Cu, the insulation not only changes into a brittle glassy phase after heat treatment but degrades current flow in the wire by 20%. Cu, from the liquid, is lost to the Ag and to Mg particles, and the additional loss to the insulation changes the composition of the outer BSSCO filaments enough to decrease their performance. The loss of Cu in the conductor creates insufficient Bi-2212 grain growth, possibly through the increase in the volume fraction of pores and Cu free phases. Although insulation provides ductility, the reactivity to the alumino silicate insulation is related to the amorphous silica content within the braid. Candidate insulation fibers without amorphous silica seem too brittle for winding. The currently used Al$_2$O$_3$-SiO$_2$ insulation for this conductor has a greater impact than previously perceived.
5.2 Future Work

First, leakage tests using yttria on the surface during the heat treatment need to be done on any new conductor to ensure that the conductor is free of surface defects. Second, more studies need to be done to understand the Cu loss from the BSCCO core to the alumino silicate insulation. This would include using the transmission electron microscope to obtain a better Cu content in the insulation. Using this Cu content data, a better estimate can be made as to how much Cu loss is felt by the outer filaments of the conductor. Quench studies on straight short samples should also be redone to examine the outer most layer of filaments in the outer bundles to see the effect of Cu loss on those regions. Third, new chemistries for insulation materials should be examined including spray and sol gel insulations. Finally, the effect of insulation on small spirals should be investigated to more closely approximate the conditions of a coil and to examine the source of the additional losses seen in coils.
LIST OF REFERENCES


Michael LoSchiavo was born of an Italian American Army officer and a German nurse. Being a military brat, he had the opportunity to see parts of the world at a young age. His parents instilled into him a work ethic that allowed him to do well in school, where he was able to complete high school in three years. Although he excelled in math and science, he always had a penchant for performance. Throughout his high school career, he balanced his studies with band, choir, and theater. As he studied at Florida State University, he leaned Mechanical Engineering during the week and acted for the film school on the weekend. Having received his Bachelors and Masters from FSU, he has a fondness for Tallahassee and has many good memories of the town and its people. He is thankful for the opportunity to work at the Applied Superconductivity Center during his Masters and for all the knowledge he has gained. But six years in one place is hard for a military child, so Michael is itching to start a new life in a place far away.