Development of High Conductivity Copper Coatings for SRF Cavity

Himal Pokhrel

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**Recommended Citation**

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DEVELOPMENT OF HIGH CONDUCTIVITY COPPER COATINGS FOR SRF CAVITY

by

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A Thesis Submitted to the Faculty of
Old Dominion University in Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

PHYSICS

OLD DOMINION UNIVERSITY
May 2022

Approved by:

Gianluigi Ciovati (Director)
Jean Delayen (Member)
Yuan Zhang (Member)
The development of metallic coatings with high purity and high thermal conductivity at cryogenic temperature could be very important for application to the superconducting radiofrequency (SRF) cavity technology. The deposition of such bulk coatings on the outer surface of a niobium cavity could result in higher heat conductance and mechanical stiffness, both of which are crucial for enhancing the cavity performance at a reduced cost.

Cold spray technology was used to deposit bulk coatings of pure copper and copper-tungsten alloys on the niobium substrate and the samples of size 2 mm × 2 mm cross section were cut and subjected to annealing at various temperatures ranging from 300 °C to 1000 °C. Thermal conductivity and residual resistivity ratio (RRR) were measured for various samples. A maximum RRR value of ∼130 and ∼40 was measured for pure Cu samples and CuW samples, respectively. Scanning electron microscopy was used to analyze the grain growth, grain distribution and presence of contaminant particulates.
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To my family.
ACKNOWLEDGMENTS

First, I would like to thank my thesis advisor, Dr. Gianluigi Ciovati of Physics Department at Old Dominion University. I had an opportunity to learn from his vast knowledge, skills, and expertise in the subject. He was very kind, patient and always supportive. I would also like to thank Dr. Pashupati Dhakal of Jefferson lab. He taught me the thermal conductivity measurement process. I am indebted to him for all his help and support. I would also like to thank Mr. Reed Beverstock of the College of William and Mary, as he taught me the process of RRR measurement using the four-point probe method. I am equally thankful to Ms. Olga Trofimova of the College of William and Mary for conducting SEM measurement on my samples. She guided me throughout the process of SEM imaging. I would also like to thank Mr. Justin Kent of SRF institute at Jefferson lab and Mr. Ishwari Parajuli, a PhD student at Old Dominion University for their help during the slow cooldown of the P4-P5 cavity. I would also like to thank Dr. Uttar Pudasaini of Jefferson lab. He helped me at various instances during the test. I would like to acknowledge Dr. Jean Delayen and Dr. Yuan Zhang as committee members of this thesis. I am gratefully indebted to them for their comments and suggestions on this thesis and for sitting on my committee.

Lastly, I would like to thank my parents for their constant encouragement. I must remember all my relatives and friends who helped me at various instances of my life. My sincerest thanks to everyone who helped me during my writing of this thesis.
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CHAPTER 1

INTRODUCTION

The use of superconducting cavities has increased in recent years due to the growing demand of particle accelerators in medical, industrial and research applications. At present, most of the cavities are made from niobium because of its high transition temperature from a superconducting to a normal state. However, bulk niobium cavities have poor thermal conductance along with other limitations, such as they have low reproducibility and only in a few instances have reached the fundamental limit of accelerating field (50 MV/m) [1].

To overcome this problem, we plan to develop a cold spray method to deposit copper on the outer surface of a superconducting radiofrequency cavity made up of bulk niobium for application in particle accelerators. Our goal is to achieve a very high thermal conductivity of the coated copper at cryogenic temperature (4.3 K). The development of such high thermal conductivity coatings with pure copper or copper tungsten alloy could be beneficial to improve the heat transfer of bulk niobium cavities for conduction cooling applications. It may also help to increase the stiffness of the bulk niobium cavity cooled by liquid helium [2].

Cold spray technology is a possible solution for the coating of SRF cavities. In this process, we deposit a desired material onto a substrate by accelerating the powder form of the material to high velocities through pressurized gas. Effective deposition of copper onto the surface of niobium requires mechanical interlocking, the extent of which is affected by various factors such as surface roughness, oxygen content, gas temperature, particle velocity etc. Since cold spray powder is deposited without melting, it reduces the risk of contaminating the surface of niobium substrate [3].

The objective of this research is to obtain niobium SRF cavities with reduced cost, increased stiffness and increased heat conductance as a result of deposition of bulk metal coatings on the outer surface of the niobium cavity. Pure copper is considered as a candidate material for cold spray deposit because of its high thermal and electrical conductivities, low processing temperature and low oxygen content [4].

I have organized this thesis in six chapters. Chapter 1 gives a brief introduction of various important topics involved in this project, such as superconductivity, SRF cavity and cold spray process. This is followed by chapter 2 which presents a brief review of some research...
papers in the related topics. Chapter 3 discusses the measurement and characterization techniques involved such as the four-point probe method, steady state technique for measuring thermal conductivity, and scanning electron microscopy. In chapter 4, I have discussed the sample preparation and measurement. Chapter 5 contains the result and discussion, and the conclusion is written in chapter 6.

1.1 FUNDAMENTALS OF RF SUPERCONDUCTIVITY

When a superconducting metal is cooled below its critical temperature, it reaches a state of zero resistance. This phenomenon is referred to as superconductivity. The term ‘state of zero resistance’ means electrical energy can be transferred with perfect efficiency, without losing anything to heat [5, 6]. Superconductivity was first discovered by H. Kamerlingh Onnes in 1911 where he observed that the electrical resistance of various metals disappeared completely below certain temperature \( T_c \), called critical temperature. The critical temperature is characteristic of each material [7]. The critical temperatures of pure metals have been observed to be below 10 K. Among the pure metals of the periodic table, niobium has the highest value of critical temperature (9.3 K) [8]. Also, various types of metallic alloys have been found to possess superconducting property.

Superconductivity involves the formation of Cooper pairs, which account for a phenomenon called Meissner effect. When a metal piece just above its critical temperature is subjected to a uniform magnetic field, the magnetic flux penetrates through the metal, thus observing the same magnetic field inside and outside the metal. However, if the temperature of the metal is lowered slightly below its critical temperature, it completely expels the magnetic field from its interior, thus behaving as a perfect diamagnet. Such a sudden creation of an opposing field inside a superconducting material is known as Meissner’s effect. This field spreads through a certain depth within the material which is known as London penetration depth (\( \lambda \)), which is given by the Eq. (2). Such expulsion of a magnetic field significantly improves the quality factor of the cavity.

The exponential decay of a magnetic field (B) inside a superconducting material can be demonstrated by the solution of the London equation:

\[
\lambda^2 \nabla^2 \vec{B} = \vec{B},
\]  

(1)
where \((\lambda)\) is known as London penetration depth, given by:

\[
\lambda = \sqrt{\frac{mc^2}{4\pi q_c^2 n_c}},
\]

where \(m\), \(q_c\) and \(n_c\) represent mass, charge and number density of charge carriers respectively.

Superconductors can be classified in two categories, namely type I superconductors and type II superconductors. Type I superconductors keep the total magnetic field until a certain value called critical field \((H_c)\) is reached. Above the critical field, the metals are completely in a normal state. They are also called low temperature superconductors. They have a low critical temperature, which typically ranges from 0 K to 10 K, and have a low and single critical magnetic field. They exhibit sharp transition from a superconducting state to a normal state.

On the other hand, type II superconductors remain in the Meissner state until a lower critical field is reached. Above this field, vortices, also called quantum of magnetic flux, start to appear. In the so-called "mixed state", a normal conducting vortex lattice is established within the superconducting matrix. The metal completely loses its superconductivity above the upper critical field. Type II superconductors are also called hard superconductors, as they do not easily loose superconductivity. They exhibit an intermediate state, called mixed state, between the lower critical field and the upper critical field \([9, 10]\). Radiofrequency (RF) cavities are the metallic chambers which are used to accelerate charged particles with the help of electromagnetic field supplied from an RF power generator. They are modeled in various shapes and sizes in such a way that the electromagnetic wave becomes resonant within the structure. The electric field in the cavity exerts a force on the charged particles, accelerating them to a higher energy. The most common example of an RF cavity is a cylindrically symmetric cavity in which the symmetry axis coincides with the beam line. An example of this is a ‘pill box cavity’.

As shown in Fig.1, the cavity supports an electric field along the axis, and a magnetic field circulates around the axis in the azimuthal direction. The electric field vector is perpendicular to the metallic surface, and the magnetic field vector is parallel to the surface. Since the magnetic field is transverse to the cavity symmetry axis in transverse magnetic (TM) modes, they are classified as \(TM_{mnp}\), where \(m\), \(n\), and \(p\) are the integers that indicate the order of mode. \(TM_{010}\) is used as fundamental mode in most cavities \([11, 12, 13]\).
In normal conducting radiofrequency cavities, such as copper cavities, the RF losses results in a large amount of heat being dissipated in the cavity walls. Therefore, they are not suitable for the applications requiring continuous-wave (cw) accelerating fields above a few million volts per meter. Superconducting radiofrequency cavities are best suited for cw, high gradient applications because their surface resistance is many orders of magnitude lower than that of copper. Also, the presence of accelerating structure causes disruption on the beam, which limits the quality of beam. SRF cavities can be designed with large beam tube diameters, reducing the impact of wakefields to the beam [14, 15]. The cavity performance is determined by several characteristic parameters, such as accelerating voltage, accelerating gradient, surface resistance, dissipated power, shunt impedance etc. I will present a brief introduction of these parameters and compare them for normal conducting cavities and superconducting cavities.

The surface resistance ($R_s$) of a normal conducting cavity is due to the skin effect, such that the RF field decreases exponentially inside the metal over the so called 'skin depth' ($\delta$).
\[
\delta = \frac{1}{\sqrt{\pi f \mu \sigma}},
\]

(3)

\[
R_s = \frac{1}{\sigma \delta},
\]

(4)

where \( f \) is the RF frequency, \( \mu \) is the magnetic permeability and \( \sigma \) is the DC conductivity. \( R_s \) can be several milliohms for a normal conducting cavity at gigahertz frequency.

In the case of superconducting cavities, there is a complete expulsion of electromagnetic fields. The current decays from the surface within the so-called London penetration depth which is of the order of a few tens of nanometer. In the presence of RF field, the unpaired electrons are not completely shielded, due to the inertia of Cooper pairs. The unpaired electrons close to the Fermi edge can be accelerated by the RF fields within the penetration depth, which results in a finite surface resistance. The surface resistance decreases exponentially with lower temperature, as the number of unpaired electrons decreases. The surface resistance of the superconducting cavity is about five orders of magnitude lower than that of normal conducting cavities [16, 17].

The dissipated power \( (P_c) \) is directly proportional to the surface resistance and is given by:

\[
P_c = \frac{1}{2} R_s \int |H|^2 \, dA,
\]

where \( H \) is the magnetic field integrated over the surface. The dissipated power is several orders of magnitude lower for a superconducting cavity than that for normal conducting cavities.

The quality factor \( (Q_0) \) is an important figure of merit for a radiofrequency cavity and is defined as the ratio of the energy stored in the cavity divided by the power dissipated in the cavity walls per radian. It is expressed as,

\[
Q_c = \frac{\omega U}{P_c},
\]

where \( \omega \) is the angular frequency of RF wave \( (2\pi f) \) and \( U \) is the energy stored in the cavity.

\( Q_0 \) is inversely proportional to the surface resistance. Generally, the \( Q_0 \) of superconducting cavities \( (10^7-10^{11}) \) is five orders of magnitude higher than that of the normal conducting cavities \( (10^3-10^5) \) [18].
1.2 NIOBIUM AS A SUPERCONDUCTING MATERIAL

Niobium is considered as the standard material for SRF cavities, mainly because of its highest critical temperature \( T_c = 9.3 \text{ K} \) and highest value of lower critical magnetic field \( H_c \) among all pure metals [19]. Various compound materials or multilayer materials have been found to have higher critical temperature and critical magnetic field, but only a few of them can be promising as alternative materials to niobium. The RF properties of bulk niobium can be summarized in Table 1 [20].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline lattice</td>
<td>b.c.c.</td>
</tr>
<tr>
<td>Electrical resistivity at 300 K</td>
<td>14.9 ( \mu \Omega \text{ cm} )</td>
</tr>
<tr>
<td>Thermal conductivity at 300 K</td>
<td>53.7 W/(m K)</td>
</tr>
<tr>
<td>Density</td>
<td>8570 kg/m(^3)</td>
</tr>
<tr>
<td>Melting point</td>
<td>2741 K</td>
</tr>
<tr>
<td>Critical field at 0 K ( H_c )</td>
<td>0.2 T</td>
</tr>
<tr>
<td>Critical temperature</td>
<td>9.3 K</td>
</tr>
</tbody>
</table>

1.3 COLD SPRAY METHOD

G. Ciovati et al. had utilized an electroplating method to grow a high-purity Cu layer on the outer surface of a niobium cavity with Nb\(_3\)Sn film on the inner surface in their recent research on SRF cavities cooled by conduction with a commercial cryo-cooler instead of liquid helium [21]. A drawback of the electroplating is the low deposition rate and the difficulty of achieving good bonding to the Nb substrate. A brief review of this paper has been made in the literature review section of chapter 2. The cold spray method can be a good alternative for the coating of copper on the niobium substrate.

Cold spray is a solid-state deposition process in which a gas called ‘propulsive gas’ is used to accelerate powder particles at supersonic velocity in order to form a coating on the surface of the substrate [22]. When solid powder particles are accelerated with a carrier gas
through a de LaValle nozzle at high-enough speed, then the particles endure plastic deformation and adhere to the surface [23, 24]. This process is called solid state process, because the process temperature is always less than the melting point of the metal powder to be sprayed. In other thermal spraying processes, the high temperature of the system may cause local heating, oxidation, phase transformation, structural change and thermal deformation, which may result in the appearance of porosity and micro-cracks in the coating. This may cause significant change in the material properties of niobium substrate, which are essential to be maintained for SRF application. The solid particles carried by the gas stream into the nozzle are accelerated by nozzle gas flow and impact the substrate. Those solid particles which impact the substrate above critical velocity will undergo plastic deformation and get bonded in a layer. As this process continues and particles form bonds with previously deposited particles, there occurs a uniform deposition with little porosity [?].

Cold spray can be classified into two categories, namely a high-pressure cold spray system and a low-pressure cold spray system. In a high pressure cold spray system, the gas stream and the powder stream enter the nozzle at a pressure above 1 MPa. This system consists of a dedicated gas compressor and generally use lighter gases, such as helium, for accelerating powder particles. On the other hand, in a low pressure cold spray system, powder feedstock is introduced directly into the supersonic diverging section of the nozzle and uses readily available compressed air or nitrogen gas for powder transport from the feeder. In this system, the powder stream is injected into the nozzle at the point where the gas has expanded to a low pressure [25]. Schematic diagrams of high pressure and low-pressure cold spray systems are shown in Fig. 2.

The two bonding methods involved in the deposition process are namely (i) interlocking of powder and substrate as a result of deformation that occurs upon impact and (ii) metallurgical bond at the coating and substrate interface, which is a chemical bond. In order to promote the bonding of material with the substrate, surface preparation of the substrate is carried out, which includes polishing, grit blasting and rinsing with pure water. The substrate preparation and optimization of the spray parameters are crucial for a good deposition of the initial layer [26].

1.4 COPPER AS A COATING MATERIAL FOR NIOBIUM CAVITY

Copper is considered as a good material to spray on niobium because of its low yield strength, ductility, and no formation of any brittle intermetallic [28]. However, it has limited solubility, significantly different melting temperature and different crystal structures than
FIG. 2. High pressure and low pressure cold spray system diagram. High pressure cold spray system has a dedicated gas compressor whereas the low pressure cold spray system uses compressed gas for powder transport. Reprinted with permission from [27].

The high ductility and high thermal conductivity of copper makes it ideal for application as a spray material. Typical mechanical, thermal, and electrical properties of a 99.99% pure copper are listed in Table 2 [31].

The presence of surface oxides in copper powder results in oxide inclusions during the spray process. Those oxides have a direct effect on the adhesion strength. The electrical and thermal properties of niobium substrate also depend on its purity, which is characterized by the residual resistivity ratio (RRR). High value of RRR suggests higher purity of the material. In general, high purity niobium has RRR value close to 300. RRR is also related to the performance of SRF cavities. I have discussed further about RRR and thermal conductivity in the next section.
TABLE 2. Physical properties of pure copper.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>8.96 g/cc</td>
</tr>
<tr>
<td>Electrical conductivity at 300 K</td>
<td>101% IACS</td>
</tr>
<tr>
<td>Coefficient of thermal expansion</td>
<td>$1.7 \times 10^{-5}$ / °C</td>
</tr>
<tr>
<td>Thermal conductivity at 300 K</td>
<td>394 W/(m K)</td>
</tr>
<tr>
<td>Melting point</td>
<td>1084 °C</td>
</tr>
</tbody>
</table>

1.5 INTRODUCTION TO THERMAL CONDUCTIVITY AND RRR

Thermal conductivity relates to the ability of a material to conduct heat. The transfer of heat involves energy transfer without any particle movement. Thermal conduction takes place when there exists a temperature difference. Thermal conductivity, $\kappa$, is an intrinsic property of a material and indicates how much heat transfer ($Q$) can take place through a given length ($L$) and surface area ($A$) of the material for a particular temperature gradient ($\Delta T$).

$$\kappa = \frac{QL}{A\Delta T}. \quad (7)$$

Wiedemann-Franz law gives the relationship between electrical conductivity and thermal conductivity of substances with freely moving electrons, i.e., metals. According to this law, the ratio of thermal conductivity to electrical conductivity of a metal at a given temperature is directly proportional to the temperature. This law is based on the kinetic theory of gases. The free electrons in the metal lattice interact with the phonon (lattice vibration) and pick up energy. When an electric field is applied, the electrons carry this energy and transport both electric charge and heat. Therefore a higher electrical conductivity corresponds to a higher thermal conductivity. Thus, the metals which are the best electrical conductors are the best thermal conductors too. The relationship between electrical conductivity and thermal conductivity is particularly important to connect thermal conductivity with the residual resistivity ratio (RRR) of a material.

The residual resistivity ratio (RRR) is defined as the ratio of electrical resistivities at room temperature (300 K) and at cryogenic temperature (4.2 K) \([32]\). The resistivity ($\rho$) of a metal of a given cross-section ($a$) and thickness ($l$) can be expressed in terms of its
resistance as:

$$R = \rho \frac{l}{a}.$$  \hspace{1cm} (8)

The ratio of resistivity at different temperatures can be expressed as the ratio of resistances at those temperatures. Thus,

$$\text{RRR} = \frac{\rho(300 \text{ K})}{\rho(4.2 \text{ K})} = \frac{R(300 \text{ K})}{R(4.2 \text{ K})}.$$  \hspace{1cm} (9)

The residual resistivity is caused by the scattering of conduction electrons in the vicinity of impurities, lattice defects and surface of the samples.
CHAPTER 2

LITERATURE REVIEW

G. Ciovati et al. [21] developed a multilayer SRF cavity with a thin Nb$_3$Sn coating on the inner surface of the niobium cavity and a thick copper coating on the outer surface. They coated a standard 1.5 GHz bulk niobium single cell cavity with a 2 $\mu$m thick layer of a Nb$_3$Sn on the inner surface and with a 5 mm thick copper layer on the outer surface for conduction cooled application. The coated cavity was tested for cavity performance at 4.3 K and 2.0 K in liquid helium. It was found that the cavity reached a peak surface magnetic field of 40 mT with a quality factor of $6 \times 10^9$ and $3.5 \times 10^9$ at 4.3 K before and after applying the thick Cu layer, respectively. The degraded quality factor ($Q_0$) after applying the thick Cu layer could be due to the differential thermal contraction between Cu and Nb, which produces strain of the film. Electroplating was used as a low-cost method to deposit a Cu layer on the outer surface of the niobium. However, its low deposition rate and difficulty of achieving good bonding to the niobium substrate are two limits of electroplating.

T. Stoltenhoff et al. [33] have done an analysis of the cold spray process and coatings. They performed a computational fluid dynamic (CFD) and an extensive spray test for the detailed analysis of the cold spray process. Their modeling and result from the experiment revealed that the adhesion occurs only when the impact velocity of the powder particles exceeds a critical velocity, which is specific to the spray material. They achieved more than 70% of deposition efficiency with nitrogen as the processing gas with the particle grain size ranging from 5 – 25 $\mu$m. The cold sprayed coating showed negligible porosity and oxygen content, as compared to the initial powder feedstock. This shows the usefulness of the cold spray process for keeping high electrical and thermal conductivities.

W. Singer et al. [34] have presented a well written document on various RRR-measurement techniques on high purity niobium. Among the various methods are DC method for RRR determination at $T_c$, DC method for RRR determination by the extrapolation of $\rho(T)$ curve to 4.2 K, AC eddy current method and AC inductive method. High thermal conductivity of the cavity wall is an essential requirement for the good performance of superconducting RF cavities. The high thermal conductivity demands high purity, which is measured in terms of residual resistivity ratio (RRR). The main factors responsible for reducing RRR are the dissolved metallic impurities, oxygen, nitrogen, hydrogen, carbon etc.
which act as the scattering centers for the unpaired electrons. The metal impurities can be aluminum, magnesium, iron, tin etc. Dislocations significantly affect the phonon contribution to the thermal conductivity. For niobium, if the phonon contribution is negligible, the residual resistivity ratio and thermal conductivity are directly proportional to each other as:

\[ \kappa = \frac{RRR}{4} \left| T = 4.2 \text{ K} \right. \]

In laboratories, RRR is used as a criterion for purity instead of thermal conductivity because, it can be easily measured using a DC 4-point probe method. In the next chapter, I will discuss in detail about the 4-point probe method of measurement of RRR.

S.S. Rosenblum et al. [35] have described an internal oxygen treatment method for producing high conductivity copper for low temperature applications. After oxygen annealing, the impurities are much less effective as scattering centers, even though the copper was less pure.
CHAPTER 3

MATERIALS AND METHODS

3.1 FOUR-POINT PROBE METHOD

In this method, current ($I$) is passed through two outer probes which results in a voltage ($V$) across the inner probes as shown in Fig. 3. The resistance ($R$) can be calculated from the I-V relation given by Ohm’s law:

$$V = IR,$$  \hspace{1cm} (11)

$$R = \frac{V}{I}. \hspace{1cm} (12)$$

For a sample of given area of cross-section ($a$) and thickness ($l$), the resistivity ($\rho$) can be related to the resistance as:

$$\rho = \frac{Ra}{l}. \hspace{1cm} (13)$$

The ratio of resistivities at 300 K and 4.3 K is equivalent to the ratio of resistance at the corresponding temperature, which can be obtained from the current-voltage curve. The four-point probe method is used to measure either bulk or thin film material. The 4-point probe set up consists of four equally spaced tungsten metal tips with finite radius, supported by springs on the other end to minimize the damage to the sample while probing. A high impedance current source is used to supply current through two outer probes, the voltage across the two inner probes is measured by a voltmeter. The set-up is enclosed inside an insulated wafer-holder and kept inside a Dewar for low temperature resistivity measurement (as low as 5 K). The four-point probe method has been described in detail in the literature \cite{36, 37}. Figure 4 shows the photograph of the 4-point probe set up for RRR measurement of our copper samples.
FIG. 3. A schematic diagram of 4-point probe measurement. Current is supplied through the two outer probes and voltage is measured across the two inner probes.

FIG. 4. Cu samples on the board for RRR measurement.
3.2 THERMAL CONDUCTIVITY MEASUREMENT

Thermal conductivities of Cu and CuW samples were measured using the steady state heat transfer method. This method involves the measurement of temperature difference between two points of the sample at a certain distance apart under the steady state heat flow through the sample. To maintain steady state flow of heat, a DC power is supplied to a heater on one side of the sample, whereas the other side is cooled by liquid helium. In this method, a sample is fitted with a heater and two temperature sensors placed at a known distance. The heater is connected to the current source in order to supply the power required for the steady flow of heat (Fig. 5). The other end of the sample is clamped to a Cu cylinder brazed to a stainless steel flange. The flange is mounted to a vacuum can, which is immersed in liquid helium. This arrangement maintains a temperature gradient between two temperature sensors, and hence a steady flow of heat takes place. By measuring the area of cross-section of the sample and the distance between the two temperature sensors, we can calculate thermal conductivity using the formula given below:

$$\kappa = \frac{Q L}{A \Delta T}.$$  \hspace{1cm} (14)

FIG. 5. Cu sample mounted for thermal conductivity measurement. Heater is connected to the top and two temperature sensors are connected at certain distance apart.
3.3 SCANNING ELECTRON MICROSCOPY

A scanning electron microscope (SEM) is a device to produce images at a significantly high resolution. It is a powerful tool for material characterization. It consists of an electron source which is generally a tungsten electron filament, a field emission gun, two electromagnetic lenses, a scanning coil and a sample chamber.

The electron source generates electrons at the top of the column and the electrons are accelerated vertically by an electromagnetic field towards the positively charged anode and hit the sample vertically. When an electron beam hits the surface of the sample, secondary electrons, backscattered electrons, and X-rays are produced which are collected by the detector and converted into a signal to produce the final image on the screen. The electron column should be under the vacuum to avoid other atoms and molecules and to increase the electron collection efficiency of the detector.

The path of the electron is controlled with the help of electromagnetic lenses. When current is passed through a coil, a magnetic field is generated. Since electrons are very sensitive to the magnetic field, their paths inside the beam column can be controlled by simply adjusting the applied current on the electromagnet. As the electrons interact with the sample, they generate various types of electrons and photons. The secondary electrons produce secondary electron (SE) images, and back scattered electrons produce BSE images. X-rays generated by the interactions are used to perform elemental analysis of the sample, which is also called energy dispersive X-ray spectroscopy (EDS) mapping, as the X-ray energy is characteristic of the element from which it was emitted [38]. SE and BSE images give the information about grain size, crystal structure and surface morphology.
CHAPTER 4

SAMPLE PREPARATION AND MEASUREMENT

4.1 SAMPLE PREPARATION

The samples consist of a niobium substrate and cold sprayed copper or copper-tungsten (CuW). We used high purity, fine grain niobium plate as a substrate. The niobium substrate was cut from a \( \sim 3 \) mm thick niobium used for SRF cavity fabrication. The cold spray was performed at Concurrent Technologies Corporation, Johnstown, PA. Copper powder with 99.5% purity and 325 mesh (particle size of \( \leq 44 \) \( \mu \)m) was used for the deposition of copper on to the surface of two \( 45 \times 70 \) mm\(^2\) and three \( 50 \) mm diameter niobium coupons. Surface preparation is very important for reliable adhesive bonding of cold sprayed coatings to the substrate. The niobium surface was first grit blasted with aluminum oxide and then cleaned with isopropyl alcohol. A raster program was used to coat the entire surface with a 1 mm step size, 200 mm/s speed and 1-inch standoff distance. The first 2 layers applied helium gas at 600 psi and 400 °C. The next 4 layers were deposited with nitrogen gas at 950 psi and 650 °C. The remainder of the deposition was done using nitrogen gas at 600 psi and 400 °C to achieve a target thickness of \( \sim 3 \) mm. Helium gas was used for the first two layers, as it allows for the Cu particles to be deposited at higher speed than nitrogen, therefore increasing the adhesion. The adhesion was measured to be \( \sim 33 \) MPa using a pull-off adhesion tester (PosiTest AT, DeFelsko), in accordance with ASTM D4541.

Figure 6 shows a picture of the cold sprayed copper sample on the surface of a niobium substrate, whereas Fig. 7 shows an optical microscopy image of the cross-section of a sample coated with similar deposition parameters as those used for this study. The microscopy images show some delamination between the deformed Cu grains, but a relatively small amount of coarse porosity.

The impurity content was measured on the samples taken from the copper powder and from the cold sprayed coupon at Applied Technical Services, Inc. The concentration of various impurities is listed in Table 3. It was found that the concentration of metal impurities such as Ag, Be, Cd, Co, Li, Mg, Mn, P, Pb, S, Se, V, Zn, and Zr was found to be \( \leq 1 \) ppm.
FIG. 6. Niobium coupon with 3 mm Cu deposited by cold spray. We used 3 circular coupons each of 50 mm diameter and 2 rectangular coupons of cross section $45 \times 70$ mm$^2$.

FIG. 7. Optical microscopy of cross-section of cold sprayed Cu on Nb surface. It shows some delaminations between the deformed copper grains.
The concentration of cold sprayed copper was measured to be 99.93%, and the concentration of copper powder was measured to be 99.96%.

After measuring the impurities content on the sample, the sample was prepared for the thermal conductivity and RRR tests. At first, the sample was cut into several identical bars each of $2 \times 2 \text{ mm}^2$ cross-sections by the method of electro-discharge machining (EDM). The samples were then subjected to vacuum annealing at different temperatures ranging from 300 °C to 1000 °C for 3 hours. Also, two samples were subjected to dry air annealing, one at 900 °C and another at 1000 °C at a pressure of about $10^{-2} \text{ Pa}$.

A powder mixture consisting of 90% by weight of tungsten and 10% by weight of copper was used for cold spray on the surface of niobium substrate to obtain the cold sprayed samples of CuW. Figure 8 shows the picture of cold sprayed CuW sample on the surface of niobium. The composition of the CuW sample was found to be 60.1 weight % of tungsten and 39.7 weight % of copper, hence the name W40Cu. This sample contained impurities.

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu sample (wt. ppm)</th>
<th>Cu-powder (wt. ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>39</td>
<td>8</td>
</tr>
<tr>
<td>O</td>
<td>565</td>
<td>362</td>
</tr>
<tr>
<td>N</td>
<td>7</td>
<td>&lt;5</td>
</tr>
<tr>
<td>H</td>
<td>29</td>
<td>6</td>
</tr>
<tr>
<td>Al</td>
<td>7</td>
<td>&lt;1</td>
</tr>
<tr>
<td>As</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Bi</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Ca</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Cr</td>
<td>2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Fe</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Ni</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Sb</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Si</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Sn</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Te</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>
such as Si (905 wt. ppm), O (760 wt. ppm), Cr (330 wt. ppm) and Zn (219 wt. ppm). After the impurity measurement, the coupon was cut by the method of electro discharge machining (EDM) into several identical samples of cross-section $2 \times 2 \text{ mm}^2$, and the small samples were subjected to annealing at various temperatures ranging from 300 °C to 800 °C for 3 hours in vacuum.

![Image of W40Cu deposited on the niobium sample by cold spray method.](image)

**FIG. 8.** Picture of W40Cu deposited on the niobium sample by cold spray method.

### 4.2 SAMPLE MEASUREMENT

Thermal conductivity was measured as a function of temperature for three Cu samples and two CuW samples. The Cu samples were as cut, annealed to 900 °C in dry air, and annealed to 1000 °C in dry air. Also, two CuW samples were measured as cut and annealed to 500 °C.

As discussed in the previous chapter, thermal conductivity was calculated from the steady state temperature difference along the sample as a function of the DC power supplied to a heater connected to one end of the sample. The other end of the sample was subjected to cooling by liquid helium. The temperature difference along the ends of the sample is used
to calculate thermal conductivity. The measured values of thermal conductivity at 4.3 K for three Cu samples and two CuW samples are listed in Table 4. A plot of thermal conductivity as a function of temperature for the three Cu samples, two CuW samples and a bimetallic NbCu sample annealed to 900 °C in dry air is shown in Fig. 9.

A plot of RRR, obtained with the 4-point probe method described in section 3.1, as a function of annealing temperature is shown in Fig. 10.

Scanning electron microscopy was performed on selected Cu samples and a NbCu sample (labeled CuNbCS1) to study their grain distribution, grain size growth and surface morphology. SEM images also help us find out contaminant particulates present on the surface of the sample. EDS analysis was done to study the elemental composition of the sample, or the impurity elements present in the sample. SEM images are shown in Figures 11 - 13 for various samples at magnification ×5k. It was observed that the grain growth occurs with increasing annealing temperature, which can be attributed to the uniform recrystallization with the increasing annealing temperature. EDS spectrum of Cu sample annealed at 600 °C for 3 hours at various spots showed the presence of oxygen and carbon. The presence of oxygen throughout the surface of the sample can be attributed to the porous nature of the surface. Carbon impurities may suggest the presence of organic matter impurities on the sample. Other impurities found were metals like zinc, iron and aluminum. A spectrum of phosphorous together with oxygen and aluminum indicates the possibility of the presence of a salt like aluminum phosphate. Metal impurities might have come while spraying or machining of the samples. Presence of other impurities can be attributed to the atmosphere

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing</th>
<th>RRR</th>
<th>$\kappa(4.3\ K)\ [W/(m\ K)]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>None</td>
<td>10</td>
<td>36</td>
</tr>
<tr>
<td>Cu</td>
<td>900 °C</td>
<td>N/A</td>
<td>233</td>
</tr>
<tr>
<td>Cu</td>
<td>1000 °C, dry air</td>
<td>132</td>
<td>345</td>
</tr>
<tr>
<td>W40Cu</td>
<td>None</td>
<td>20</td>
<td>43</td>
</tr>
<tr>
<td>W40Cu</td>
<td>500 °C</td>
<td>39</td>
<td>94</td>
</tr>
</tbody>
</table>
FIG. 9. Thermal conductivity of various samples as a function of temperature. The variation of thermal conductivity ($\kappa$) with temperature was measured on the cold sprayed Cu samples annealed at various temperatures; Cu annealed at 900 °C is represented by red curve, Cu annealed at 1000 °C is represented by gray curve, and as cut Cu is represented by green curve), the copper-tungsten samples (orange curve represents as cut W40Cu and blue curve represents W40Cu annealed at 500 °C), and the Nb sample with the cold sprayed copper (black curve). The highest value of $\kappa$ was measured for the copper sample annealed to 1000 °C.

or surrounding environment. Other major impurities revealed from EDS spectra (Figs. 14 and 16) and FESEM images (Fig. 15) include metals such as tin, lead, silica etc.

1Field Emission Scanning Electron Microscope images. FESEM produces images at very high magnification of the order of 100K.
FIG. 10. RRR as a function of annealing temperature. Blue circles represent cold sprayed Cu and red squares represent W40Cu samples. For Cu, RRR increases with annealing temperature and becomes maximum at 1000 °C, whereas for W40Cu, RRR is maximum at 500 °C.
FIG. 11. SEM image at $\times 5k$ of Cu sample annealed to 300 $^\circ$C. The grains are very small in size and the grain boundaries are not clearly visible. Some porosity can be noticed from the image.
FIG. 12. SEM image at ×5k of Cu samples annealed to 600 °C. The grain size increases with the increase in annealing temperature thus reducing porosity. The grain boundaries are clearly visible.
FIG. 13. SEM images at ×5k of Cu samples annealed to 900 °C. The large grain size is due to the uniform re-crystallization that takes place with the increase in annealing temperature.
FIG. 14. EDS (Energy-dispersive X-ray spectroscopy) spectrum of Cu sample annealed at 600 °C inside grain boundary. It shows Cu as a sole component with a little presence of oxygen and carbon at the grain boundary.
FIG. 15. FE SEM image of impurities in Cu sample annealed at 600 °C.
FIG. 16. EDS spectrum near the impurity in the Cu sample annealed at 600 °C. The impurity could be the salt of phosphorous, aluminium, lead, and oxygen, such as lead phosphate or aluminium phosphate.
CHAPTER 5

RESULT AND DISCUSSION

For the cold spray purpose, we used copper powder which had about two order of magnitude higher oxygen concentration than specified for oxygen-free copper. This is because a high purity (~99.99%) copper with suitable mesh size for cold spray is not readily available. The higher oxygen concentration on the copper sample can also be confirmed from the EDS analysis. The low electrical and thermal conductivities of the as deposited sample, as shown in Table 4, also result from the presence of high density of lattice defects and porosity. Annealing was performed to increase the RRR and thermal conductivity of the cold sprayed copper samples [39]. Annealing at 1000 °C for 12–92 hours in a dry air atmosphere was found, in particular, to enhance RRR by about one order of magnitude [35]. This finding was confirmed in our samples. It can be seen from Table 4 that the Cu-sample annealed to 1000 °C in dry air atmosphere has the highest RRR and highest value of thermal conductivity at 4.3 K among the tested samples, followed by the Cu sample annealed to 900 °C in dry air.

Since the copper cold spray is also intended to be applied to a niobium cavity coated with a thin film of Nb3Sn on the inner surface, the post-annealing of the cavity with the cold sprayed copper layer above 950 °C may cause significant tin sublimation which may degrade the superconducting properties of the Nb3Sn film. Therefore, the annealing temperature should be limited to 900 °C. We also measured the thermal conductivity of a NbCu bimetallic sample annealed at 900 °C for 3 hours. Its thermal conductivity at 4.3 K was a factor of 3 higher than that of the pure niobium substrate with RRR value of 300.

High thermal and electrical conductivity of cold sprayed copper annealed to 900 °C is also supported by the SEM images, which show a continuous grain growth in the sample with the increase in annealing temperature from 300 °C to 900 °C. The cold sprayed copper sample undergoes uniform recrystallization with the increase in annealing temperature. This process results in the increase of grain size, which helps to fill the voids present along the grain boundary, thus decreasing porosity.

The low temperature electrical and thermal conductivities of the cold sprayed copper-tungsten (CuW) samples are less affected by annealing. There was an increase in RRR with annealing temperature below 500 °C, which could be due to the inhomogeneous grain
growth of copper and tungsten components [40, 41]. Copper-tungsten samples exhibited highest RRR value at the annealing temperature of 500 °C. Above this temperature, there occurs a grain growth of tungsten component which causes more porosity in the sample, thus leading to a decrease in RRR. A niobium cavity with a thin film of Nb₃Sn on the inner surface will be coated with a cold sprayed copper on the outer surface and post annealed at 900 °C, and it will be tested after being cooled to ~ 4 K using a commercial cryo-cooler.
CHAPTER 6

CONCLUSION

Cold sprayed copper samples post annealed in dry air have shown significant increase in the thermal conductivity at 4.3 K and RRR values for an annealing temperature as high as 1000 °C. However, the annealing temperature should be limited to 900 °C if copper is to be cold sprayed on the outer surface of a niobium SRF cavity which has Nb₃Sn thin film on the inside surface. This is because post annealing of the cavity with cold sprayed copper layer above 950 °C may cause significant phase transition of tin, resulting in the degraded superconducting properties of the Nb₃Sn film. This result encourages us to carryout copper cold spray on the niobium cavity with a Nb₃Sn thin film and post anneal to 900 °C for enhanced performance of the cavity in conduction cooled applications.
BIBLIOGRAPHY


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Himal Pokhrel was born in Pyuthan district of Nepal. He obtained bachelor’s degree in physics from Tribhuvan University, Nepal and a Master’s degree in Physics from A. P. Goyal Shimla University, India. He moved to the United States in the Fall of 2019, and was admitted to the graduate program of Physics at Old Dominion University. He worked at the SRF institute of Thomas Jefferson National Accelerator Facility (TJNAF) as a graduate research assistant under the supervision of Dr. Gianluigi Ciovati.