Chapter 1

This chapter is devoted to the brief introduction to superconductivity and its various properties explained theoretically. Fundamental features of YBCO and BSCCO high-temperature superconductors along with various synthesis methods have also been discussed briefly.

1.1 Introduction to superconductivity

A superconductor is a metal or alloy that conducts electric current with zero or negligible resistance ($\rho$) when cooled below a certain temperature. The temperature where this transition takes place is known as the critical temperature ($T_c$) as shown in figure 1.1.

![Figure 1.1: The resistance versus temperature for a non-superconductive metal and a perfect superconductor.](image)

This phenomenon was first discovered by Dutch physicist Heike Kamerlingh Onnes in 1911 following his success in liquefaction of helium on 10 July 1908 [1.1]. The first superconducting element discovered by H. K. Onnes was mercury (Hg) which exhibited a resistivity from 0.03 $\Omega$ to $3.0 \times 10^{-6}$ $\Omega$ within a temperature range of 0.01 K when cooled to liquid helium temperature at 4.2 K as shown in figure 1.2. Later, several other metallic elements and compounds like Pb ($T_c = 7.19$ K), Nb ($T_c = 9.26$ K), Nb$_3$Sn ($T_c = 18.3$ K), Nb$_3$Ga ($T_c = 20.3$ K), Nb$_3$Ge ($T_c = 23.2$ K), etc. were discovered.
Collectively all these elements and compounds are called “low temperature superconductors (LTS)” as these are cooled with LHe. Usage of liquid helium makes the superconductive applications much expensive and limited.

An experimental breakthrough in superconductivity happened in 1986 when George Bednorz and Alex Muller found a lanthanum based brittle ceramic Ba-La-Cu-O compound superconducting [1.2] at temperatures of $T_c = 30$ K. At that time, such temperatures were believed before to be forbidden for superconduction. Soon after this discovery, in 1987, M. K. Wu and C. W. Chu replaced lanthanum with yttrium created a superconductor and called it YBCO superconductor. This superconductor has a critical temperature as high as $T_c = 93$ K [1.3]. These were economically attractive since such temperatures are above the boiling point of liquid temperature ($LN_2$) which is 77 K. Thus it leads to cheap and easily affordable coolant for superconductors compared to expensive helium. Subsequently, other compounds like BSCCO ($T_c = 110$ K) [1.4], TBCCO ($T_c = 125$ K) [1.5], Hg-based cuprates HgBa$_2$Ca$_2$Cu$_3$O$_{8+y}$ ($T_c = 135$ K, at high pressure of 30 GPa $T_c = 164$ K and at 18 kbar $T_c = 250$ K) [1.6–1.9] etc. were discovered. These discoveries started the era of high-temperature superconductivity. Recently in 2008, Japanese scientists have discovered the iron-based layer compound LaO$_{1-x}$F$_x$FeAs with $T_c$
~ 43 K for $x = 0.11$ and at ~ 4.0 GPa mechanical pressure [1.10]. All these compounds are termed “high temperature superconductors (HTS)”.

1.2 Properties of superconductor

Low temperature superconductors have several interesting properties. Walter Meissner and Robert Ochsenfeld discovered in 1933 the expulsion of magnetic flux from the interior of the material in the superconducting state. As the superconductor is cooled below the critical temperature, the applied external magnetic field does not penetrate completely [1.11]. This phenomenon is known as perfect diamagnetism and is in general referred to as the “Meissner effect”. Until that, it was thought that the superconducting state was completely governed by the electrical resistivity $\rho = 0$. Thus, the superconduction is a phase state like the liquid and solid states of the water and depends on the temperature and magnetic field. It is characterized by two distinctive properties: 

perfect electrical conductivity ($\rho = 0$) and perfect diamagnetism ($B = 0$ inside the superconductor), as shown in Figures 1.1 and 1.3 respectively.

![Diagram of Meissner effect](image)

Figure 1.3: The Meissner effect: the expulsion of a weak, external magnetic field from the interior of a superconductor. The field is applied (a) at $T > T_c$ and (b) at $T < T_c$.

In order to explain the Meissner effect, a phenomenological model was proposed by the London brothers, Fritz and Heinz in 1935. They explained the Meissner effect by proving that the superconductivity was a consequence of the minimization of electromagnetic free energy in the supercurrent [1.12]. The London equations for a superconductor are expressed as
\[ \frac{\partial j_s}{\partial t} = \frac{n_s e^2}{m} E \]  
\[ \nabla \times j_s = -\frac{n_s e^2}{mc} B \]

where \(j_s\) is the supercurrent, \(e\) is the charge of an electron & proton, \(m\) is the electron mass, \(c\) is the velocity of the light and \(E\) & \(B\) are the electric and magnetic fields respectively. These two equations are derived based on the two-fluid model which assumes that all free electrons are divided into two groups: superconducting electrons of density \(n_s\) and normal electrons of density \(n_n\). Thus, the total density of free (conduction) electrons is \(n = n_s + n_n\). As the temperature increases up to \(T_c\), \(n_s\) decreases from \(n\) to zero as shown in figure 1.4 (a). The first London equation (1.1) can be interpreted as Newton’s second law for the superconducting electrons. It follows from this equation that in the stationary state i.e. when \(dj_s/dt = 0\), there exists no electrical field inside the superconductor. The second London equation (1.2) when combined with the Maxwell equation, \(\text{curl } B = 4\pi j/c\), leads to

\[ \nabla^2 B = \frac{1}{\lambda_L^2} B \]  
\[ \lambda_L = \sqrt{\frac{mc^2}{4\pi n_s e^2}} \]

is called as the London penetration depth. For a one-dimensional case, the solution of the equation (1.3) can be represented as

\[ B_z(x) = B_0 e^{-x/\lambda_L} \]
where ‘$B_0$’ is the magnitude of magnetic field outside the superconductor when applied parallel to the surface. This implies that the magnetic field is exponentially screened from the interior of a superconductor with penetration depth ($\lambda$) as shown in figure 1.4 (b).

![Figure 1.4: (a) electron density inside the superconductor, (b) the penetration of the magnetic field into the superconductor.](image-url)

At $x = \lambda_L$, the magnetic flux density decrease by $1/e$ which is roughly 63%. Since the penetration depth ($\lambda_L$) is directly related to the superfluid density ‘$n_s$’ which is temperature dependent, an approximation for the temperature dependence of $\lambda_L$ is given by the empirical formula

$$\lambda(T) = \frac{\lambda(0)}{\left[1 - (T/T_c)^4\right]^{1/2}}$$

where $\lambda(0)$ is the penetration depth at $T = 0$ K.

L. V. Shubnikov and coworkers [1.13] theoretically discovered Vortices in superconductors in 1937. They found an unusual behavior i.e. the existence of two critical magnetic fields for some superconductors in external magnetic fields. They also discovered a new state of superconductors, known as the mixed state or the Shubnikov phase.

V. Ginzburg and L. Landau proposed an extension to that proposed by London’s in order that explains superconductivity much better. The Ginzburg-Laudau (G-L) theory
[1.14] explained the behaviour of the super-electron by a pseudo-complex wave function 
\( \Psi(r, t) = |\Psi(r)| e^{i\theta(t)} \) with the superfluid density \( n_s = 2 |\Psi(r)|^2 \). Under these assumptions, 
**Ginzburg-Laudau equations** are expressed as

1st GL equation (1.7)

\[
\alpha \Psi + \beta |\Psi|^2 \Psi + \frac{1}{4m} \left( \hbar \nabla + \frac{2e}{c} A \right)^2 \Psi = 0
\]

2nd GL equation (1.8)

\[
j = \frac{e}{m} |\Psi|^2 \left( \hbar \nabla \varphi - \frac{2e}{c} A \right) = 2e |\Psi|^2 v_s
\]

where \( v_s \) is the superfluid velocity, \( A \) is the magnetic vector potential such that \( \mathbf{B} = \text{curl} (A) \) is the magnetic field, \( m \) is the effective mass of an electron, \( e \) is the charge of an electron, \( j \) is the electrical current density. Here \( \alpha \) and \( \beta \) are the phenomenological parameters and are temperature dependent. They are chosen such that free energy is minimized when the order parameter \( |\Psi| \) is finite and below \( T_c \) and become zero for \( T > T_c \). This implies that the expansion of \( \alpha \) must have a zero'th order term that is equal to zero at \( T = T_c \) where as for \( \beta \) the zero-order term \( \beta_0 \) is finite. Thus \( \alpha \) and \( \beta \) are in generally expressed as \( \alpha(T) = \alpha_1(T - T_c) \) and \( \beta(T) = \beta_0 \) where \( \alpha_1, \beta_0 \) are two constants. The two characteristic (physical) lengths that occur in a superconductor have been derived from above two G-L equations are (a) the Ginzburg-Landau Coherence length (\( \xi \)) and (b) the Ginzburg-Landau penetration depth \( (\lambda_{G-L}) \). The \( \xi \) is written as

\[
\xi = \sqrt{\frac{\hbar^2}{4m|\alpha|}}
\]

(1.9)

\( \xi \) characterises the size of thermodynamic fluctuations in the superconducting phase. The penetration depth \( (\lambda_{G-L}) \) is written as

\[
\lambda = \sqrt{\frac{mc^2}{8\pi e^2 |\varphi_0|^2}} = \sqrt{\frac{mc^2 \beta}{8\pi e^2 |\alpha|}}
\]

(1.10)

where \( \varphi_0 \) is the equilibrium value of the order parameter \( |\Psi| \) in the absence of an electromagnetic field that characterises the depth of penetration of an external magnetic field can penetrate the superconductor. The ratio \( \kappa = \lambda / \xi \) is a dimensionless parameter
and is known as *Ginzburg-Landau parameter*. The Ginzburg-Landau parameter can be represented in terms of known quantities as

\[ \kappa = 2 \sqrt{2} H_c \lambda^2 \frac{e}{\hbar c} \]  

where \( H_c \) is the critical magnetic field. This parameter \( \kappa \) depends on the properties of the materials and further characterizes the superconductor.

In the same year in 1950, E. Maxwell [1.15] and C. A. Reynolds [1.16] found the *isotope effect* in superconductors that shows the way to the correct theory of superconductivity in metals. A study of different superconducting isotopes of mercury established a relationship between the critical temperature \( T_c \) and the isotope mass \( M \) as 

\[ T_c M^{1/2} = \text{constant} \]  

This turned out to be valid for most of conventional superconductors.

In 1957, the microscopic theory of superconductivity was formulated by John Bardeen, Leon N Cooper and John Robert Schrieffer [1.17 - 1.18]. This famous theory is now known as the *BCS theory* that is based on the interaction of a "gas" of conducting electrons with elastic waves of the crystal lattice (phonons). Two electrons in a vacuum repel each other by the Coulomb force, but in a superconductor below the critical temperature \( T_c \) there is a net attraction between two electrons forming the so-called *Cooper pair*. Each Cooper pair consists of two electrons of opposite momenta and spins. Based on this concept, BCS ground state of a superconductor is expressed as

\[ |\text{BCS}\rangle = \prod_k \left( u_k^2 + v_k e^{i\phi} b_k^+ \right) |0\rangle \]  

where \( u_k^2 \) and \( v_k^2 \) are the probability functions satisfying the condition \( u_k^2 + v_k^2 = 1 \). \( \phi \) represents the phase of the order parameter and \( |0\rangle \) represents the vacuum state. The operator \( b_k^+ = c_{k\uparrow}^+ + c_{-k\downarrow}^+ \) creates a pair of electrons of opposite spins and momenta and represents Fermion creation operators obeying Fermion anti-commutation relations for spin \( (\uparrow\downarrow) \) electrons. Based on this assumption that all electrons in a superconducting...
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State near the Fermi surface are correlated in pair with equal and oppositely directed
momenta and spin, a model Hamiltonian as per the BCS theory is written as

\[ H_{BCS} = \sum_{k, \sigma} \varepsilon_k c_k^{\dagger} c_k - \sum_{k, k'} V_{kk'} c_k^{\dagger} c_{-k'}^{\dagger} c_{-k} c_{k'} \]  

The first term of this equation denotes the superconducting energy of electrons forming
the Cooper pairs while the second term is the translation of the phonon mediated electron-
electron interaction. \( V_{kk'} \) is the strength of the pairing interaction and is generally taken
independent of \( k, k' \). Since the Hamiltonian is bilinear in the fermionic operators, using
Bogoliubov-transformation, the BCS gap-equation can be expressed for the ground state
as

\[ \Delta_k = -\sum_{k'} V_{kk'} \frac{\Delta_{k'}}{2E_{k'}} \]  

where the associated energy is \( E_k = (\xi_k^2 + \Delta_k^2)^{1/2} \) and \( \xi_k \) is the energy of a quasi-particle
excitation above the Fermi surface for a normal Fermi liquid. For the weak-coupling case
where \( V_{kk'} = -V \) within the cut off frequency \( \omega_c \approx \omega_D \) (Debye frequency), the energy gap
width \( \Delta \) in the quasi particle spectrum when \( T \rightarrow 0 \) is obtained as

\[ \Delta = 2\hbar \omega_D \exp \left( -\frac{1}{N(0)|V|} \right) \]  

where \( \hbar \omega_D \) is the Debye energy, \( N(0) \) is the density of energy state on the Fermi
surface and \( |V| \) is the interaction energy of two quasi-particles. Similarly, the finite-T
BCS gap equation is derived as

\[ \Delta_k = -\sum_{k'} V_{kk'} \frac{\Delta_{k'}}{2E_{k'}} \tanh \left( \frac{\beta E_{k'}}{2} \right) \]  

where \( \beta = \frac{1}{k_BT} \). At the critical temperature \( T_c, \Delta \rightarrow 0 \) and \( \beta = \beta_c \) so that the solution of the
equation (1.16) is derived as

\[ k_B T_c = 1.14 \hbar \omega_D \exp \left( -\frac{1}{N(0)|V|} \right) \]  

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Thus the gap at zero temperature and the critical temperature has a universal ratio in BCS theory expressed as

\[
\frac{2\Delta(0)}{k_BT_c} = 3.528
\]  

(1.18)

This ratio is close to the result measured for simple elementary superconductors. For superconductors with stronger coupling, such as mercury, and for unconventional superconductors this equation is not in good agreement. In case of strong-coupling superconductors, a modified BCS-McMillan’s expression for \(T_c\) [1.19] is given as

\[
T_c = \frac{\Theta_D}{1.45} \exp \left( -\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right)
\]

where \(\Theta_D = h\omega_D / k_B\) is the Debye temperature, \(\lambda \approx C / M \langle \omega^2 \rangle\) is the electron-phonon coupling constant and ‘C’ is a constant for a given class of materials, \(M\) is the mass and \(\langle \omega^2 \rangle\) is the mean-square average phonon frequency, \(\mu^*\) is a renormalized Coulomb repulsion. The values of \(\lambda\) are known to range from \(\leq 0.10\) to \(\geq 2.0\) while the parameter \(\mu^*\) is assigned a value in the range \(0.10 - 0.15\) whose precise value is not too important unless \(T_c\) is very low.

Brain D. Josephson in 1962 theoretically predicted the Quantum-mechanical tunneling of Cooper pairs through a thin insulating barrier (~ few nanometers thick) between two superconductors. This was subsequently known as Josephson effects [1.20]. Josephson predicted that the current through a junction would be a sine function of the difference ‘\(\varphi\)’ between the phases \(\theta_1\) and \(\theta_2\) of the two superconductors on either side of the weak link. Based on this prediction, the Josephson equations are expressed as

\[
I = I_c \sin \varphi \quad (\varphi = \theta_1 - \theta_2)
\]

(1.20)

and

\[
\nu = \frac{\hbar}{2e} \frac{d\varphi}{dt}
\]

(1.21)
where $I_c$ is the Josephson critical current. This is also the maximum current the structure can support without dissipating power and $V$ is a constant voltage applied across the junction. Due to this nonzero voltage maintained across the tunnel barrier, an alternating supercurrent would flow through the barrier in addition to the DC current produced by the tunneling of single electrons. The frequency $f_J$ can be derived as

$$f_J = \frac{2eV}{\hbar}$$  \hspace{1cm} (1.22)

These above two effects are known as the DC and AC Josephson effects and play a special role in superconducting applications.

Based on the above properties, superconductors can be classified based on a number of criteria such as material types, elements or compounds, transition temperature, penetration depth, coherence length etc. There is another way to classify them is from the response of the superconductor responds to an applied external magnetic field which can also be predicted by the Ginzburg-Landau parameter ($\kappa$). Superconductors are classified into two main types depending on the value of ‘$\kappa$’. Type-I superconductors have $\kappa < 1/\sqrt{2}$ while Type-II superconductors have $\kappa > 1/\sqrt{2}$.

1.2.1 Type –I superconductors

Type–I superconductors are those who lose their superconductivity very easily or abruptly when placed in the sufficiently strong external magnetic field. All superconducting elements and some of their alloys except Niobium (Nb) and Vanadium (V) are type-I superconductors. The variation of the critical field $B_c$ with temperature for a type-I superconductor is approximately parabolic and is expressed as

$$B_c(T) = B_c(0) \left[1 - \left(\frac{T}{T_c}\right)^2\right]$$  \hspace{1cm} (1.23)
where $B_c(0)$ is the value of the critical field at absolute zero. The dependence of $B_c(T)$ is schematically shown in the figure 1.5(a). The penetration depth and coherence length for type-I superconductors are shown in the figure 1.5(b). The figure 1.5(b) shows that the penetration depth is shorter than the coherence length for Type-I superconductors.

Figure 1.5: (a) Critical magnetic field as a function of temperature for Type-I superconductors, (b) the penetration depth and coherence length for Type-I superconductors.

1.2.2 Type -II superconductors

Type-II superconductors are those who lose their superconductivity gradually but not abruptly when placed in the external magnetic field. In the case of Type-II superconductors, there are two critical fields, the lower critical fields $B_{c1}$ and the upper critical fields $B_{c2}$, as shown in the figure 1.6(a). For the applied external field $< B_{c1}$, the superconductor completely expels the field and behave like a Type-I superconductor. At fields just above $B_{c1}$, the magnetic flux begins to penetrate partially into the material until the upper critical field $B_{c2}$ is reached. Above $B_{c2}$ the material completely looses their superconductivity and reaches to the normal state. Also in Type-II superconductors, figure 1.6(b), the penetration depth is longer than the coherence length.
Figure 1.6: (a) Critical magnetic field as a function of temperature for Type-II superconductors, (b) the penetration depth and coherence length for Type-II superconductors.

Between $B_{c1}$ and $B_{c2}$, the superconductor is in the mixed state. In this region, the magnetic flux partially penetrates the material in the form of microscopic filaments called vortices that forms a regular (triangular) lattice. Each vortex consists of a normal core in which the magnetic field is large, surrounded by a superconducting region, and can be approximated by a long cylinder with its axis parallel to the external magnetic field. Inside the cylinder, the superconducting order parameter ($\psi$) is zero. The radius of the cylinder is of the order of the coherence length ($\xi$). The number of vortices gradually increases as the field is raised from $B_{c1}$ to $B_{c2}$ ($n = B / \phi_0$, $n$ is the density of vortices, $\phi_0 = h / 2e = 2.0679 \times 10^{-15}$ Tm (or Weber) is the magnetic flux quantum). The lower and upper critical fields for Type-II superconductors [1.21-1.22] can be expressed in terms of known parameters as

$$H_{c1} \approx \frac{\phi_0}{\pi \lambda^2}$$ (1.24)

and

$$H_{c2} \approx \frac{\phi_0}{\pi \xi^2}$$ (1.25)

This equation implies that there will be only one vortex within a region of $\pi \xi^2$. 
Apart from the temperature and external magnetic field, the normal and superconducting state of a material is also determined by the current density flowing through the material. Thus, for the occurrence of superconductivity in a material the temperature must be below the \textbf{critical temperature} \((T_c)\), the external magnetic field must be below the \textbf{critical field} \((B_c)\) and the current density flowing through the material must be below the \textbf{critical current density} \((J_c)\). The three parameters \(T_c (H, J), B_c (T, J)\) and \(J_c (H, T)\) define a critical surface as illustrated in the figure 1.7. Beneath the surface the material is in superconducting state and above the surface the material is in normal state.

![Figure 1.7: Illustration of superconducting critical surface.](image)

The usefulness of a superconductor for technological applications depends on its ability to carry sufficient high current density without resistive losses at the working field \((B)\) and temperature \((T)\). There are two limits to the \(J_c\) in practical superconductors: the intrinsic \(J_c\) is limited by \(H_{c2}, H_{irr}\) (irreversible magnetic field) and flux pinning, and the extrinsic \(J_c\) limited by factors like grain connectivity, grain orientation (anisotropy).
1.2.3 High Temperature Superconductors

Till 1986, all the known superconductors have their critical temperatures below 23 K. These are only cooled using liquid helium (LHe). Liquid helium has been expensive and also needs care in handling. A research laboratory in Zurich made a breakthrough using metal oxides as superconductors. Bednorz and Muller [1.2] in 1986 found that Lanthanum copper oxide \((\text{La}_x \text{Ba}_y \text{Cu}_z \text{O}_w)\) has critical temperature of 30 K. This discovery led to a new interest in this class of high temperature superconductors (HTS) known as cuprates that consist of copper-oxygen planes. The critical temperature was increased to 90 K, above the liquid nitrogen temperature of 77 K, with the discovery of yttrium barium copper oxide \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\), known as YBCO or Y-123 in 1987. This was a major breakthrough as superconductivity. For cooling purpose, liquid nitrogen (LN2) is being used. It is cheaper and much safer than liquid helium. Later on bismuth oxides \(\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}\) and \(\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}\) abbreviated as Bi-2212 and Bi-2223 were discovered and at present is one of the most advanced HTS materials. These two compounds are also referred to as BSCCO, which stands for bismuth strontium calcium copper oxide.

Further thallium and mercury based cuprate superconductors were discovered. Thallium family of high-temperature superconductors are referred to as TBCCO having the general formula \(\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}\) and a mercury family HBCCO having general formula \(\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}\). Since the presence of copper-oxygen (CuO\(_2\)) planes has an influence in these cuprate families, few compounds along with their critical temperatures are listed in the table 1.1 [1.23].

<table>
<thead>
<tr>
<th>Cuprates</th>
<th>CuO(_2) planes</th>
<th>Critical temperature T(_c) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{La}<em>{1.87}\text{Sr}</em>{0.13}\text{Cu}<em>O</em>{4.8})</td>
<td>1</td>
<td>38</td>
</tr>
<tr>
<td>(\text{Tl}_2\text{Ba}_2\text{Cu}_O_6)</td>
<td>1</td>
<td>80</td>
</tr>
<tr>
<td>(\text{YBa}_2\text{Cu}<em>O</em>{6.92})</td>
<td>2</td>
<td>93.7</td>
</tr>
<tr>
<td>(\text{LaBa}_2\text{Cu}<em>3\text{O}</em>{7-\delta})</td>
<td>2</td>
<td>97</td>
</tr>
<tr>
<td>(\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}<em>2\text{O}</em>{8+\delta})</td>
<td>2</td>
<td>95</td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th>Materials</th>
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<th>3</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl2Ba2CaCu2O8</td>
<td>110</td>
<td>130</td>
<td>135</td>
</tr>
<tr>
<td>Tl2Ba2Ca2Cu3O10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HgBa2Ca2Cu3O8+δ</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Since BSCCO and YBCO HTS materials are the most studied cuprate superconductors and are widely used HTS, some of their critical parameters are listed in the table 1.2.

Table 1.2: Critical parameters of YBCO, Bi-2212 and Bi-2223 HTS.

<table>
<thead>
<tr>
<th>Critical parameters</th>
<th>YBCO</th>
<th>Bi-2212</th>
<th>Bi-2223</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$ (K)</td>
<td>93</td>
<td>87</td>
<td>110</td>
</tr>
<tr>
<td>$B_{irr}$ (T) at 4.2 K</td>
<td>$&gt;30$</td>
<td>$&gt;30$</td>
<td>$&gt;30$</td>
</tr>
<tr>
<td>$B_{irr}$ (T) at 77 K</td>
<td>$&gt;5$</td>
<td>0.005</td>
<td>0.5</td>
</tr>
<tr>
<td>$J_c$ (A/mm²) at 4.2 K</td>
<td>$&gt;1,00,000$</td>
<td>5,000</td>
<td>3,000</td>
</tr>
<tr>
<td>$J_c$ (A/mm²) at 4.2 K</td>
<td>$&gt;10,000$</td>
<td>100</td>
<td>500</td>
</tr>
</tbody>
</table>

Cuprates still remained as a high priority due to its high $T_c$ until the discovery of superconductivity in iron-pnictides by a collaborative group at the Tokyo Institute for Technology led by Yoichi Kamihara [1.24]. They discovered that the CuO plane is not an absolute requirement for superconductivity. Today, the highest critical temperatures are approaching 200 K. This is almost over two thirds of the way to achieving a superconducting material with a critical temperature that can be achieved without cooling. Common features of the HTS are that they are usually superconductors of type-II with a ceramic structure, and with large anisotropy in their superconducting properties. They have very low values of $B_{c1}$ (few mT) and very high value of $B_{c2}$ (hundreds of T).

1.2.4 Intermediate Temperature Superconductors

Magnesium diboride (MgB$_2$) is an ionic binary compound with a simple hexagonal crystal structure (AlB$_2$ type structure). It was first synthesized and its structure was confirmed in 1953 [1.25]. This compound remained ideal on the laboratory shelves for decades. In 2001, Japanese researchers measured the transition temperature of magnesium diboride to be 39 K [1.26], far above the highest $T_c$ of any of the elemental or...
binary alloy superconductors. While 39 K is still well below the \( T_c \)'s of the "warm" ceramic superconductors, subsequent refinements in MgB\(_2\) have paved the way for its use in industrial applications. MgB\(_2\) is a type-II superconductor and its maximum critical currents (\( I_c \)) under different applied magnetic fields are \( 10^5 \) A/m\(^2\) at 20 T, \( 10^6 \) A/m\(^2\) at 18 T, \( 10^7 \) A/m\(^2\) at 15 T, \( 10^8 \) A/m\(^2\) at 10 T and \( 10^9 \) A/m\(^2\) at 5 T [1.27]. MgB\(_2\) is the first superconductor which showed two distinct energy gaps in the superconducting state. The two energy bands arise from the \( \sigma \) (formed from the \( sp^2 \) hybrids of boron \( 2s \) and \( p_{x,y} \) orbitals) and \( \pi \) (originated from the boron \( p_z \) orbital) bands.

Laboratory testing has found MgB\(_2\) will outperform NbTi and Nb3Sn wires in high magnetic field applications like MRI. In 2006, a 0.5 tesla open MRI superconducting magnet system was built using 18 km of MgB\(_2\) wires. This MRI used a closed-loop cryocooler, without requiring externally supplied cryogenic liquids for cooling [1.28-1.29].

1.3 Fundamental Properties of YBCO and BSCCO

1.3.1 Fundamental Properties of YBCO

Yttrium barium copper oxide (YBCO) compound is the first high temperature superconductor to be superconducting above the liquid nitrogen (N\(_2\)) temperature 77 K at 1.0 atmosphere. During its fabrication, it was observed that the oxygenation procedure of YBCO samples has played an important role. In other words, the superconducting properties of \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{\gamma} \) are sensitive to the value of \( \delta \), its oxygen content. YBCO is formed with oxygen content close to 6 and then has to undergo the phase transition from a tetragonal to orthorhombic material, including the characteristic formation of twin boundaries [1.30-1.32]. Only those materials with \( 0 \leq \delta \leq 0.65 \) are superconducting below \( T_c \), and when \( \delta \sim 0.07 \) the material superconducts at the highest temperature of 95 K [1.33] or in highest magnetic fields: 120 T for B perpendicular and 250 T for B parallel to the CuO\(_2\) planes [1.34].
Silver-cladded YBCO wires [1.35-1.36] are difficult to be fabricated in practice as high-angle grain boundaries is present in the bulk materials of YBCO. However deposition of YBCO on flexible metal tapes with buffering metal oxides overcomes such limitations. These types of YBCO tapes on Ni or similar substrates reach values of the critical current density, $J_c$ of $10^6$ A/cm² at 77 K (self-field) and lengths of about a meter [1.37].

1.3.2 YBCO Structure

The YBCO superconductors have layered perovskite-like and highly anisotropic crystal structure as shown in the figure 1.8. The boundary of each layer is defined by planes of square planar CuO₄ units sharing 4 vertices. Perpendiculars to these CuO₂ planes are CuO₄ ribbons sharing 2 vertices. The yttrium atoms are found between the CuO₂ planes, while the barium atoms are found between the CuO₄ ribbons and the CuO₂ planes. The $Y_1Ba_2Cu_3O_7$ compound [1.38] has both orthorhombic ($\delta < 0.5$) and tetragonal ($\delta \geq 0.5$) structures with the superconducting phase that has an orthorhombic structure.

Figure 1.8: Structure of $Y_1Ba_2Cu_3O_7$ compound.
The structure of these materials depends on the oxygen content. When $\delta = 1$, the O(1) sites in the Cu(1) layer are vacant and the structure is tetragonal. The tetragonal form of YBCO is insulating and does not superconduct. Increasing the oxygen content slightly causes more of the O(1) sites to become occupied. For $\delta < 0.65$, Cu-O chains get formed along the b-axis of the crystal. The Y and two Ba ions get ordered along the c-axis and the other O vacancy occurs in the Y-plane. Elongation of the b-axis changes the structure to orthorhombic symmetry with lattice parameters of $a = 3.8185 \text{ Å}$, $b = 3.8856 \text{ Å}$, and $c = 11.6804 \text{ Å}$. Optimum superconducting properties occur when $\delta \sim 0.07$ and all of the O(1) sites are occupied with few vacancies.

1.3.3 Fundamental Properties of BSCCO

Bismuth strontium calcium copper oxide (BSCCO) is a high-temperature superconductor represented as $\text{Bi}_2\text{Sr}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{2n+1+\delta}$, with $n = 0, 1, 2$ and 3. BSCCO is the first high-T$_c$ superconductor which does not contain a rare earth element. Based on the numbers of the metallic ions present, BSCCO is abbreviated as BSCCO-2201 or Bi-2201 or simply Bi2201 and so on. The critical temperatures $T_c$'s of BSCCO compounds are 34 K for Bi-2201 [1.39], 90 K for Bi-2212 [1.40], 110 K for Bi-2223 [1.41] and 110 K for Bi-2234 [1.42].

BSCCO is a type-II superconductor. The upper critical field in BSCCO polycrystalline samples at 4.2 K has been estimated as 200±25 T [1.43]. BSCCO needs to be completely doped by a partial cation substitution (e.g. Pb for Bi) or an excess of oxygen atoms in order to be superconducting. This is usually done by adding interstitial oxygen atoms to the copper oxide plane. $T_c$ is sensitive to the exact doping level i.e. the maximum $T_c$ for Bi-2212 is achieved with an excess of about 0.16 holes per Cu atom [1.44]. $T_c$ is also sensitive to the duration of the sintering process [1.45]. Four layers of Ag-sheathed Bi-2223 tapes of more than 25 km in length, each tape having an average critical current of approximately 118 A d.c. at 77 K has been manufactured and tested for power cable project [1.46].
1.3.4 BSCCO Structure

BSCCO is a cuprate superconductor, an important category of high-temperature superconductors sharing a two-dimensional layered (perovskite) structure with superconductivity taking place in copper oxide planes. BSCCO has 1, 2 or 3 CuO planes, with $T_c$ increasing with the number of planes. The compounds have layered structures parallel to the crystallographic $a$, $b$ plane, consisting of rocksalt like BiO bilayers that alternate with perovskite-like $[\text{Sr}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{2n+3}]$ units. The $n = 1$ and $n = 2$ members of the homologous series may be described as double BiO layers that alternate with $[\text{Sr}_2\text{CaCu}_2\text{O}_5]$ and $[\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_7]$ units, respectively. The $[\text{Sr}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{2n+3}]$ units contain CuO$_2$ sheets, formed by corner-sharing [CuO$_4$] units, which are oriented parallel to the $a$, $b$ plane. The 2201 phase is characterized by one CuO$_2$ sheet ($n = 0$), and the 2212 and 2223 phases by two and three CuO$_2$ sheets ($n = 1$ and $n = 2$), respectively. Thus, the general structure of all members of the series consists of CuO$_2$ sheets that are separated by calcium (for $n > 0$) and covered in the $c$-direction by SrO sheets. Figure 1.9 shows the crystallographic structure of the most commonly studied member Bi-2212.

These perovskite-like units alternate in $c$-direction with the BiO bilayers. An incommensurate modulation is exhibited in these phases in the direction of the crystallographic $b$-axis. The spacing of this superstructure is about 4.74 times that of the $b$-axis parameter with the space group $P_{cmm}$ or $P_{nnm}$ [1.47]. This superstructure is formed by a modulation of the BiO bilayers, which results in a regular alternation of the structure of the BiO bilayers [1.48]. Due to the significantly different parameters of the $a$, $b$ axis and $c$-axis, the crystallization rate in direction of the $a$, $b$ plane is about 1000 times faster than in the $c$-direction. Thus, the crystals have a mica-like leafy shape, exhibiting a pronounced cleavability parallel to the $a$, $b$ plane due to the weak bonding between the neighbouring BiO layers. This structure also implies a pronounced anisotropy of the properties, causing the so-called “two-dimensional superconductivity” parallel to the $a$, $b$ plane.
Figure 1.9: The unit cell of Bi-2212. Bi-2201 has one less CuO$_2$ in the top and bottom half and no Ca layer of Bi-2212 unit cell while Bi-2223 has an extra CuO$_2$ and Ca layer in each half of Bi-2212 unit cell.

1.4 Coated Conductors and Thin Films

Due to higher working temperatures above LN$_2$, now-a-days, two superconducting materials i.e. BSCCO and YBCO tapes are preferred for the different electric power applications such as power transmission cables, power transformers, fault current limiters, motors and generators. BSCCO tapes are produced in lengths up to thousands of meters with reproducible properties whereas YBCO tapes are in rapid development, the
production length and reproducibility still lower than for the 1st generation tapes. Recent achievements of critical currents exceeding 1.0 MA/cm² at 77K in YBCO deposited over suitably textured substrates have stimulated interest in potential applications of coated conductors at high temperatures and high magnetic fields. This superior performance has been shown in small laboratory samples of coated high temperature superconductors. Efforts are focused on scaling-up the processing on a continuous basis while minimizing any degradation of wire performance. Continuous manufacturing of long wires or tapes will require reel-to-reel type of processing which consists of (a) preparation of substrate material, (b) preparation and application of the seed and buffer layer(s), (c) preparation and application of the HTS material and required post-annealing and (d) preparation and application of the passivation / stabilization / insulation layer.

1.4.1 First and Second Generation Tapes

One of the main challenges in developing high-performance superconductors has been the brittleness of many of the most promising materials and drawing them into wires that can carry current. Recent developments allow fabrication of superconductor wires and tapes due to their flexibility and high current carrying capacities. The most commonly used materials in early HTS were bismuth-based, specifically Bi-2212 and Bi-2223. These materials have come to be known as first generation (1G) superconductors and have been used to demonstrate a variety of HTS power devices. Performance benefits of these HTS devices compared to conventional, non-superconducting devices have been demonstrated for all these applications. At present, textured tapes and wires of BSCCO superconductor are commercial available in long lengths (~ kilometers), although its actual use is restrained to low field applications or temperatures below 25 K due to its irreversibility line.

The second kind of tapes (coated conductors) are called as second generation (2G) superconductors, which are based on yttrium barium copper oxide (YBCO) compounds. This 2G conductor offers both performance (operation at higher temperatures and background magnetic fields) and cost benefits. In film form of 1 μm of thickness,
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YBCO is capable of transporting high critical currents in the order of $3 \text{MA/cm}^2$ at 77 K and $H_{\text{ext}} = 0$.

1.4.2 Substrates

Good quality superconducting coated conductor can only be obtained if its layer is grown on the right substrate and buffer layers. The substrate must have the following essential properties [1.49] such as (a) chemical compatibility, (b) similar thermal expansion coefficient, (c) good matching between the different crystallographic cells, (d) low roughness and must be flexible and hard and (e) cheap and available in long lengths. For coated conductor the substrate needs to have a metallic base over which other buffer layers can be grown epitaxially prior to the superconducting phase.

The buffer layers are used to avoid unwanted reactions between film and substrate. Hence the buffer layer must be chemically compatible with both materials. Some reaction between the buffer layer and substrate may be permissible if it is confined to a region near the interface. If the thermal-expansion mismatch between the HTS layer and substrate is large, a buffer layer with intermediate thermal properties may alleviate cracking of the film. Choosing a buffer material with a lattice constant intermediate between the two materials may improve the epitaxial quality of the grown layer. There are two different basic architectures of YBCO coated conductors, where the texturing processes are either applied on the metallic substrate or on a ceramic buffer layer grown on a polycrystalline metallic substrate. The two mostly used techniques for growth on metallic substrates are (a) IBAD and (b) RABITS techniques.

1.4.2.1 IBAD technique

Ion-Beam-Assisted-Deposition (IBAD) technique is a material engineering technique which combines ion implantation with simultaneous sputtering or another physical vapor deposition technique as shown in the figure - 1.10. Besides providing independent control of parameters such as ion energy, temperature and arrival rate of atomic species during deposition, this technique is especially useful to create a gradual transition between the substrate material and the deposited film, and for depositing films
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with less built-in strain than is possible by other techniques. These two properties can result in films with a much more durable bond to the substrate. Experience has shown that some meta-stable compounds like cubic boron nitride (c-BN) can only be formed in thin films when bombarded with energetic ions during the deposition process.

![Figure 1.10: Schematic diagram of the ion beam assisted deposition (IBAD) system.](image)

Figure 1.10: Schematic diagram of the ion beam assisted deposition (IBAD) system.

Ion bombardment causes changes in the properties and the crystal structure of thin films. The experiments were generally performed after the films were deposited, rather than during deposition. In many instances, the damage induced by random collisions of the ions with the lattice led to a decrease in the crystalline texture. Films grown without simultaneous ion bombardment had no preferred orientation. A preferred crystal orientation was observed for films grown during bombardment. However, no more specific description was made of these “preferred” orientations.

In this process, an insulating buffer layer (YSZ, MgO, GZO or La$_2$Zr$_2$O$_7$) is deposited on polycrystalline metallic substrates (Inconel, hastelloy, Ni or stainless steel). Once the textured template IBAD buffer layer is obtained, a YBCO layer can be grown epitaxially onto this buffer layer by using Pulsed Laser Deposition (PLD) or BaF$_2$ Ex-situ process or TFA-MOD Process etc. Then, the ion beam induced texture is transferred to the superconductor. Additionally, some extra buffer layers can be grown between the
IBAD-textured layer and the YBCO in order to enhance crystallographic coupling between different layers and avoid chemical reactivity. Perovskite buffer layers such as SrTiO$_3$ (STO), BaZrO$_3$ (BZO) and SrRuO$_3$ (SRO) are used and also a fluorite buffer of CeO$_2$ which forms an excellent template for YBCO growth. Figure 1.11 shows a schematic of the typical layer architecture in an IBAD coated conductor.

![Schematic diagram of biaxially aligned YBCO coated conductor using an IBAD textured buffer layer.](image)

Good superconducting properties for YBCO deposited directly on IBAD MgO / Si$_3$N$_4$ / Alumina was demonstrated [1.50]. Also on Ni-alloy substrate platforms, good YBCO superconducting properties have been reported using thin (<250 nm) buffer layers of YSZ / Y$_2$O$_3$ [1.51] or YSZ / CeO$_2$ [1.52] between the IBAD MgO and the final YBCO overcoat. The buffer layers deposited between the IBAD MgO template and the final YBCO film have not been optimized to the extent that they have been for buffer layers on IBAD YSZ templates.

### 1.4.2.2 RABiTS technique

The rolling-assisted-biaxially-textured-substrates (RABiTS) technique is shown schematically in the figure 1.12. Biaxially textured Ni substrates are formed by consecutive rolling of a polycrystalline, randomly oriented high-purity (99.99%) bar to total deformations greater than 90% followed by recrystallization. Ni is chosen over Cu because of its greater resistance to oxidation. By controlling the surface condition of the
work rolls, it was possible to obtain substrates with surfaces as smooth as those obtained by mechanical and chemical polishing. Average line scans in a 50 × 50 μm region indicate an rms roughness of ~10 nm. The surface condition of a substrate can greatly affect the epitaxy and integrity of buffer layers and hence the \( J_c \) of the superconducting film. Obtaining substrates with surfaces adequate for film growth without the need for a cumbersome polishing step is important for scale up to long lengths. Subsequent annealing of the substrates in a wide temperature range (after recrystallization at 1000 °C for 4 h in a vacuum \(~10^{-6}\) torr) results in the formation of a sharp \( \{100\}\langle100\rangle \) cube texture. The texture was found to be stable up to the melting point of Ni.

![Diagram of RABiTS process](image)

Figure 1.12: Schematic of the Rolling-assisted biaxially-textured substrates (RABiTS) process.

After recrystallization at 1000 °C, the average grain size is approximately equal to the thickness of the substrate (in this case ~125 μm). Thus, the substrate can be thought to be comprised of a columnar structure of grains, with the columns aligned with the (100) plane parallel to the surface of the columns and the [100] direction aligned along the rolling direction. In order to grow high-quality epitaxial superconducting films on the
biaxially textured Ni substrate, a chemical and structural buffer layer is required. Typically, the desired buffer layers for 123 film growth are oxides. Hence, the task of fabricating a suitable substrate for epitaxial deposition of the superconductor involves epitaxial deposition of oxide buffer layers on Ni. This is difficult because of the ease of surface oxide formation on Ni under the typical oxidizing conditions required for oxide film growth. Although the surface oxide on (100) Ni can be epitaxial, it typically forms a (111) textured NiO layer, the orientation of which is unsuitable for fabricating high-Jc 123 films since many high-angle boundaries are present.

There are two proven successful methods in producing cube-on-cube epitaxial oxide buffer layer films on rolled and recrystallized Ni. The first involves epitaxial deposition of noble metal layers on Ni followed by deposition of oxides and the second involves deposition of oxides directly on Ni under reducing conditions.

In the first route, noble layers such as Pd, Pt, Ag, etc. are epitaxially deposited on the base metal using sputtering and electron beam evaporation. Oxide buffer layers are then epitaxially deposited using laser ablation on the noble metal surface which has a diminished tendency to oxidize. Three configurations of RABiT substrate have been investigated using this route. Multilayer structures ML0, ML1 and ML2 have been fabricated as indicated schematically in the figure 1.13.

![Diagram of RABiT structures](image)

Figure 1.13: Schematic representations of cross-sections of four RABiT multilayer structures, ML0, ML1, ML2 and ML3.
In the second route to obtaining (100) epitaxy oxides on Ni, oxide deposition is performed under reducing conditions by introducing H₂ gas during the initial film growth (the corresponding multilayer configuration is ML3). CeO₂ was deposited directly on textured Ni. Deposition was performed under a partial pressure of hydrogen, p(H₂), such that NiO is unstable, while CeO₂ is stable though oxygen deficient. After the initial stage of CeO₂ deposition, the remaining CeO₂ was deposited under oxidizing conditions to a total thickness of 0.5 μm. Since the as-deposited layer tended to crack along the [100] and [010] directions, a 0.5 μm thick YSZ layer was epitaxially deposited at the same temperature. A 1.4 μm 123 film was then deposited at 780 °C in an O₂ pressure of 185 mtorr. After deposition, the film was cooled at 10 °C/min and the O₂ pressure was increased to 700 torr at 400 °C.

Thus RABiTS appears to be a promising and industrially scalable method to fabricate long-lengths of high performance superconductors. Using this method, critical current densities exceeding 3 MA/cm² have been demonstrated for YBCO films [1.53], Ic/width approaching 300 A/cm width in thick films have also been demonstrated. Most importantly, reel-to-reel, continuously fabricated epitaxial YBCO/RABiTS have Ic’s over 1 MA/cm² and Ic’s of ~ 130 A in 8 meter long lengths, showing the viability of this process. Efforts are presently underway world-wide to achieve large-scale manufacturing of high performance and low-cost conductors using this process.

1.4.3 Methods of YBCO Film Growth

There are various physical and chemical methods widely used for the synthesis of YBCO superconducting films out which only few synthesis techniques like pulsed laser deposition (PLD) process, BaF₂ Ex-situ process and TFA-MOD process are discussed here in more details.

1.4.3.1 PLD process

The principle of pulsed laser deposition (PLD) process is based on the evaporation of the target material inside a vacuum chamber subjected to a high power laser beam pulses as shown in the figure 1.14. Each of these pulses causes a complete vaporization of
a small volume of material in the area of the beam spot on the target surface (in a plasma plume) which deposits it as a thin film on a substrate. This process can be carried out in ultra-high vacuum or in the presence of a background gas such as oxygen which is commonly used when deposited films has to be fully oxygenated. However, this process of PLD can generally be divided into the following four individual steps as (a) ablation and plasma formation, (b) plume propagation, (c) deposition of the ablation material on the substrate and (d) nucleation and growth.

![Figure 1.14: Sketch of pulsed laser deposition (PLD) process for fabricating YBCO superconductors.](image)

During **ablation and plasma formation**, the laser pulse penetrates into the surface of the material within the penetration depth, typically 10 nm for most materials depending on the laser wavelength and the index of refraction of the target material at the applied laser wavelength. This process occurs within 10 ps of a ns laser pulse. The surface of the target is then heated up and the material is vaporized. For a given laser energy density at the target surface, ablation using a KrF excimer laser (248 nm, ≈30 ns pulse duration) resulted in far superior film of Y$_1$Ba$_2$Cu$_3$O$_{7-δ}$. 

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During plume propagation, the material expands in a plasma parallel to the normal vector of the target surface towards the substrate due to Coulomb repulsion and recoil from the target surface. The spatial distribution of the plume is dependent on the background pressure inside the PLD chamber. The density of the plume can be described by a $\cos^2(\theta)$ law with a shape similar to a Gaussian curve. The most important consequence of increasing the background pressure is the slowing down of the high energetic species in the expanding plasma plume. It has been observed that particles with kinetic energies around 50 eV can resputter the film already deposited on the substrate. This result in a lower deposition rate and can furthermore result in a change in the stoichiometry of the film.

During deposition of the ablation material on the substrate, the high energetic species ablated from the target are bombarding the substrate surface and may cause damage to the surface by sputtering off atoms from the surface but also by causing defect formation in the deposited film. The sputtered species from the substrate and the particles emitted from the target form a collision region, which serves as a source for condensation of particles. When the condensation rate is high enough, a thermal equilibrium can be reached and the film grows on the substrate surface at the expense of the direct flow of ablation particles and the thermal equilibrium obtained.

During nucleation and growth, the film depend on several growth parameters like laser energy, ionization degree of the ablated material, the stoichiometry, the deposition flux, surface temperature, surface roughness and background pressure. It is observed that the nucleation density increases when the deposition flux is increased. Also it is observed that the nucleation density decreases as the substrate temperature is increased [1.54]. To ensure stoichiometric transfer from the target to the film an oxygen background is needed. If the oxygen background is too low, the film will grow off stoichiometry which will affect the nucleation density and film quality [1.55]. Y. Iijima's group (Fujikura Ltd.) reported on a 9.6 m long carrying an $I_c = 50$ A (1.0 cm tape width), corresponding to a current density $J_c = 0.42$ MA/cm$^2$. On a shorter length of 8 cm (for which the buffer layer was deposited at a slower rate), $I_c = 140$ A (1.0 cm tape width, corresponding to $J_c = 1.2$ MA/cm$^2$ was measured [1.56].
1.4.3.2 BaF$_2$ Ex-situ Process

In BaF$_2$ ex-situ process, the precursor film is performed in a high-vacuum apparatus. This vacuum chamber includes electron guns for Y and Cu sources and a thermal heater for BaF$_2$ as shown in the figure 1.15(a). In this process, stoichiometric amount of Y, Cu and BaF$_2$ is co-evaporated onto a substrate at room temperature. Then the precursor film is converted into YBCO at an elevated temperature in a controlled atmosphere as shown in the figure 1.15(b). The precursor film is heated up to a conversion temperature of 740 °C in a humidified reduced-oxygen environment of 70 Torr H$_2$O and 130 mTorr O$_2$.

![Figure 1.15: (a) Schematic for deposition of precursor film using the BaF$_2$ process. (b) Schematic of typical oxifluoride decomposition / YBCO conversion schedule used in the ex-situ processing of YBCO conductors.](image)

The film will be annealed in this humidified environment to a sufficient longer time so that the metal-oxifluoride is fully decomposed and HF is released completely. Once this process is completed, the environment is switched to “dry” to ensure that YBCO formation will proceed to completion without degradation due to moisture. Then the sample is cooled to room temperature. The RABiTS architecture used for coatings with the BaF$_2$ process consist of a 50mm thick Ni-3%W metal tape (Ni-W) coated with a
Ni overlayer (1.5mm), and Y$_2$O$_3$ (0.2mm), YSZ (0.15mm), CeO$_2$ (0.015mm) buffer layers. Additionally, YBCO films grown by the BaF$_2$ process on IBAD YSZ templates with a Hastelloy substrate coated with a CeO$_2$ buffer layer have also been analysed. All these samples have been prepared at the Oak Ridge National Laboratory (USA) by Dr. Feenstra [1.57].

1.4.3.3 TFA-MOD Process

Trifluoroacetates-metal organic deposition (TFA-MOD) process [1.58] is a low cost process for mass production of coated conductors because it is a non-vacuum process. The basic TFA-MOD process, figure 1.16, consists of four distinct steps: (1) precursor solution synthesis, (2) precursor solution coating, (3) pyrolysis of the organic material, and finally (4) YBCO nucleation and growth.

![Figure 1.16: Schematic of steps during the TFA-process from the as-deposited precursor layer to the crystallized YBCO layer.](image)

During the precursor solution synthesis, trifluoroacetates are formed from metal (Y, Ba, Cu) acetates dissolved in de-ionized water and trifluoroacetic acid. The resulting aqueous solution is refined to yield a glassy blue gel and dissolved in methanol to form the final coating solution.

During the precursor solution coating, deposition of the TFA precursor solution onto single crystals or flexible metallic substrate is carried out by spin coating process or dip coating. The solution so prepared is coated on the single crystal substrate of LaAlO$_3$(1 0 0) with a size of 10 mm square at 4000 rpm by the spin coating technique and on the
CeO$_2$ buffered IBAD($Zr_2Gd_2O_7$) / Hastelloy tape with the 10 cm long by the dip coating technique. In the spin-coating system, the coating solution is dripped onto a substrate and the solvent vaporized from the coating solution on the turning substrate to give a gel film.

During the pyrolysis, the thermal decomposition of the metalorganic salts and removal of the organic constituents of the precursor takes place leaving behind a mixture of nominally copper oxide, yttrium oxide, and barium fluoride. The process is carried out in a humid, oxidizing atmosphere at temperatures of $\sim 400$ °C. The thermal decomposition of TFA precursor films results more than 50% reduction in film thickness and is accompanied by an increase of stress within the film and is very susceptible to cracking at decomposition temperatures. In order to reduce cracking in the film, the original temperature-time profile developed for the decomposition required nearly 20 hours.

During nucleation and growth of YBCO, the reaction of BaF$_2$ in the precursor film with H$_2$O takes place which requires transport of H$_2$O vapour into the film and removal of the resulting HF product. As the BaF$_2$ reacts, the YBa$_2$Cu$_3$O$_{6.5}$ phase nucleates at the buffer interface and continues to grow through the film thickness. Precise control of the reaction rate is required to promote the epitaxial nucleation of YBa$_2$Cu$_3$O$_{6.5}$ on the substrate (oxide buffer) surface and subsequent growth of the highly textured YBa$_2$Cu$_3$O$_{6.5}$ through the thickness of the film. As the film approaches the hold temperature (725 – 850 °C), the YBa$_2$Cu$_3$O$_{6.5}$ begins to nucleate at the substrate (buffer) interface. The YBa$_2$Cu$_3$O$_{6.5}$ continues to grow through the thickness of the precursor as the film is held at the growth temperature. Finally, the film is slow cooled to $\sim 450$ °C into a dry oxygenizing atmosphere to carry out the film oxygenation and thus transform the insulating tetragonal (YBa$_2$Cu$_3$O$_{6.5}$) to the superconducting orthorhombic (YBa$_2$Cu$_3$O$_{7.5}$) phase.

Further to achieve a high orientation of superconducting layer and prevention of the reaction with metal substrate, a suitable buffer layers have to be considered. The combination of CeO$_2$ on IBAD-YSZ is considered as an effective buffer to satisfy a high acid resistivity and high crystal grain alignment. The CeO$_2$ buffer layer was deposited on
IBAD-YSZ / Hastelloy substrates by RF magnetron sputtering. From XRD analysis, the CeO$_2$ buffer layer showed very good in-plane alignment on YSZ-IBAD buffer layer. In a holding time of 1 h, the suitable maximum heat treatment temperature was found to be from 750°C to 775°C for TFA-Y123 on metal substrate. The $J_C$-$B$ property of Y123 on CeO$_2$/YSZ/Hastelloy shows the $J_C$ values of 1.4 MA/cm$^2$ at 77.3 K, 0 T and more than $10^5$ A/cm$^2$ at 77.3 K, 2 T. The high performance under high magnetic field was also confirmed [1.59].

1.4.4 Methods of BSCCO Film Growth

There are four major techniques used to manufacture BSCCO conductors such as (1) powder in tube method, (2) dip coating and other ceramic coating methods, (3) deposition of biaxially textured thin films on textured buffer layers or substrates and (4) bulk growth techniques. Here only power-in-tube method is discussed in details.

1.4.4.1 Powder-In-Tube process

The powder-in-tube (PIT) [1.60-1.61] process was one of the first to be developed for processing of Bi-2212 and Bi-2223 into conductor. The schematic sketch involving the different steps is shown in the figure 1.17.

Silver tube filled with HTS powder is extruded / drawn as a wire of the diameter about 1-2 mm. The choice for tube material is silver or a silver alloy due to its oxygen diffusion properties, good mechanical properties, non-reactivity with HTS core material, reduction of the melting point of Bi-based HTS materials during thermal processing and final forms a template upon which the HTS material can grow. For multifilament conductor, the wire is drawn in a hexagonal shape, cut into shorter lengths and formed into a stack of 7, 19, 37, 55, 61, 85 or higher numbers of filaments. This stack is then inserted in another tub, and the composite is extruded or drawn to wire. The restacking and redrawing steps are omitted for monofilament wire. For round wire, the final step is heat treatment, but most conductors are made in a flat “tape” format achieved by rolling the wire to an aspect ratio of ~10:1.
Bi-2212 is subjected to a partial melt process at 800-900°C to form large grains of that compound with the crystallographic a-b planes (i.e. the Cu-O planes that have a high critical current density) oriented parallel to the current flow direction of the tape and to the wide face of the tape. Both Bi-2223 and Bi-2212 are highly anisotropic materials and the $J_c$ within the a-b plane may be several orders of magnitude larger than $J_c$ along the c-axis. Obtaining good uniaxial (c-axis) orientation of the grains in these two materials is necessary to achieve high $J_c$. Bi-2223 also undergoes a heat treatment (800-840°C) at the tape stage, but then usually goes through one or more additional rolling / heat treatment cycles. The mechanical properties of such wire did not allow bending it on small radius because of the ceramic structure of the filaments. Thermal and electrical stability of such wires is extremely high because of the silver matrix. On the other hand, the high price of the silver limits the cost reduction of these wires.

The irreversible field at 4.2 K is very large both for Bi-2212 and Bi-2223. However the critical current density of Bi-2223 decreases faster in applied field than for Bi-2212. At 4.2 K Bi-2212 can carry up to 1,000 A/mm$^2$ in fields of 26 T while the
corresponding current density of Bi-2223 is lower. That is why Bi-2212 is preferred for HTS magnet applications at 4.2 K. At temperatures above 20 K, the performance of Bi-2212 is strongly degraded due to important flux creep and at 77 K its irreversible field is only 0.005 T. On the other hand, Bi-2223 at 77 K has its irreversible field of 0.5 T which is not of interest for magnet design but is good enough for transport current applications. Therefore, Bi-2223 is at present the most widely used material for wires and cables, operated at 77 K.

Bibliography


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[1.53] John E. Mathis, Amit Goyal, Dominic F. Lee, Fred A. List, M. Paranthaman, David K. Christen, Elliot D. Specht, Donald M. Kroeger and Patrick M. Martin, Biaxially Textured YBa$_2$Cu$_3$O$_{7-\delta}$ Conductors on Rolling Assisted Biaxially Textured Substrates with Critical
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