Chapter 4

Preparation and characterization of MgB$_2$ wires and tapes

This chapter describes the preparation and characterization of MgB$_2$ superconductor in mono and multifilamentary wire and tape geometries. Over the years many techniques were developed for making LTS and HTS materials into wires and tapes. Of these, Powder-In-Tube (PIT) method is an easy and scalable method for large scale production of long length conductors. For MgB$_2$ also PIT is the most preferred for long length fabrication. In the present study also chose *in situ* PIT method for the preparation of MgB$_2$ wires and tapes as the method is most efficient for large scale industrial production of long length conductors.

In PIT method, the precursor powder is filled into suitable metallic tubes, mechanically rolled/extruded/drawn into desired size and shape followed by a heat treatment. In the case of MgB$_2$, the metallic sheath chosen must be chemically compatible with MgB$_2$ and should not degrade the superconductivity. It must be non-reactive with Mg, B and MgB$_2$. The sheath metal must have adequate strength to give mechanical support to the brittle superconducting core, but also must be ductile enough to withstand the mechanical working. The metal sheath has to play a role of diffusion barrier for the volatile and reactive Mg. Several sheath materials such as Cu, Ag, Ni, Nb, Ti, Fe and some alloys like SS, monel (Cu-Ni) are tried for
MgB$_2$. Of these most of the sheath materials form intermetallics or solid solutions with Mg/B, affecting the superconducting properties of the system to different extents depending on the reactivity [60].

In order to select a suitable sheath material, we carried out a systematic study of the reactivity of the commonly available sheath materials such as Fe, SS, Cu, Ag, Ni and Ta by mixing their fine powders with stoichiometric Mg and B and heat-treating the reaction mixtures at different temperatures. The studies showed that among the above metals only Fe, SS and Ta are acceptable for use as sheath materials for MgB$_2$ wire/tape fabrication. In the present work MgB$_2$ based wires and tapes were fabricated in both mono and multifilamentary geometries using Fe as the sheath material.

4.1 Reactivity of sheath materials with Mg/B

4.1.1 Experimental Details

The samples for reactivity study were prepared by in situ Powder-In-Sealed-Tube (PIST) method as detailed in chapter 3. Commercially available seamless stainless steel (SUS 304) tubes of 10 cm length with an outside diameter (OD) of 10 mm and inside diameter (ID) of 8 mm were used for the study. Stoichiometrically weighed and uniformly mixed Mg powder and amorphous B powder, added with a 10 wt.% sheath material powder viz. Ag, Cu, Fe, Ni, SS and Ta (99% purity, -200 mesh) were packed into the tubes, compacted mechanically and end-sealed by arc welding. Thirty such samples (five each with six different sheath material powders) were prepared and each set was subjected to heat treatment at 600 °C, 675 °C, 750 °C, 825 °C and 900 °C for 2 hours.

4.1.2 Characterizations

The phase analysis of the samples were performed by using powder XRD. Phase identification of the samples were performed using X’pert Highscore Software in support with ICDD-PDF-2 database. Quantitative phase analysis of the samples were carried out from the XRD. Microstructural examination and elemental analysis of the samples were done by using a scanning electron microscope (SEM-JEOL JSM 5600LV) equipped with an X-ray energy dispersive spectrometer (EDS).
4. Preparation and characterization of MgB\(_2\) wires and tapes

### 4.1.3 Results and discussion

Figure 4.1 shows XRD patterns of the various sheath material viz. Ag, Cu, Fe, Ni, SS and Ta added samples heat treated at different temperatures viz. 600, 675, 750, 825, 900 °C for 2 h. The XRD measurements were performed on the ground cores, taken out by mechanically peeling off the SS sheath. From all the XRD patterns, it can be seen that MgB\(_2\) formation is almost complete in all samples at around 825 °C and small peaks corresponding to MgO are also present.

For the Ag added sample (figure 4.1 a), reaction between Mg and Ag starts even at the temperatures of 600 °C. At 600 °C reaction between Mg and Ag forms an intermetallic Ag\(_{0.24}\)Mg\(_{0.76}\), and after 750 °C, the Ag\(_{0.24}\)Mg\(_{0.76}\) fully converts into MgAg, reducing the effective superconductor volume. Above 750 °C the amount of MgAg phase is considerable and some of the peaks are very strong and sharp. The presence of Ag-Mg phases strongly impede the flow of super-currents from grain to grain, causing a decrease of current carrying capacity of the system [60].

For the Cu added sample (figure 4.1 b), the competition in reaction among Mg, Cu and B led to different phase formations. Significant Mg-Cu reaction took place even at 600 °C resulting in the formation of the binary phase Mg\(_2\)Cu. As the reaction temperature is increased above 750 °C, Mg\(_2\)Cu undergoes partial decomposition and releases a part of the Mg and this results in a phase composition of MgCu\(_2\). Thermodynamically, the Gibb’s free energy of MgCu\(_2\) is lower than that of Mg\(_2\)Cu and this explains the formation of MgCu\(_2\) which is more stable at higher reaction temperatures. There were reports on the deleterious effects of MgCu\(_2\) formation in Cu sheathed conductors at temperatures above 750 °C [163–165]. These reactive phases both Mg\(_2\)Cu and MgCu\(_2\) act as obstacles to the supercurrent flow, creating weak links among MgB\(_2\) grains.

For the Fe introduced sample, Fe remains inert towards both Mg and B at temperatures up to 825 °C (figure 4.1 c). For the 900 °C heat treated sample, the intermetallic compound Fe\(_2\)B begins to form due to reaction of Fe with boron. Being highly brittle in nature Fe\(_2\)B worsens the mechanical and conduction properties of the superconductor. Studies by Grovenor et al [166] showed the formation of Fe\(_2\)B at temperatures in excess of 850 °C. However, the best \(J_C\) for MgB\(_2\) wires are generally obtained with Fe as the
Figure 4.1: Powder XRD pattern of sheath material viz. (a) Ag, (b) Cu, (c) Fe, (d) Ni, (e) SS and (f) Ta added samples heat treated at different temperatures.

sheath material [167, 168], for relatively low temperature (< 850 °C) heat treated wires/tapes wherein the reaction between Fe and Mg/B is minimal.
Ni added samples showed significant reaction at temperatures as low as 600 °C causing the formation of Mg₂Ni (figure 4.1 d). At higher temperatures, boron also take part in the reaction process resulting in the formation of the tertiary compound MgNi₂.₅B₂ in large quantities. Bellingeri et al [169] observed a thick reaction layer of MgNi₂.₅B₂ by neutron diffraction at the Ni-MgB₂ interface while fabricating monofilamentary tapes.

Mg and B are found to be exceptionally inert with respect to stainless steel even up to the highest heat treatment temperature of 900 °C (figure 4.1 e), suggesting the chemical compatibility of SS for MgB₂ wire fabrication. It may be recalled that SS tubes were used for preparing all the samples in this study. However, not even a trace of any reacted phase is observed in any of the samples under the extreme heat treatment conditions used. No chemical reactions have been observed for the Ta introduced in situ processed samples up to a temperature of 825 °C (figure 4.1 f). At higher temperatures, Ta begins to react with B forming TaB₂ inside the core. The results of reactivity of in situ processed MgB₂ with various sheath materials at different temperatures are summarized in Table 4.1.

Table 4.1: Reaction products of Mg/B with various sheath materials.

<table>
<thead>
<tr>
<th>Sheath</th>
<th>Heat treatment temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>600 °C</td>
</tr>
<tr>
<td>Ag</td>
<td>Ag₀.₂₄Mg₀.₇₆</td>
</tr>
<tr>
<td>Cu</td>
<td>Mg₂Cu</td>
</tr>
<tr>
<td>Ni</td>
<td>Mg₂Ni, MgNi₂.₅Bi₂</td>
</tr>
<tr>
<td>Fe</td>
<td>No reaction</td>
</tr>
<tr>
<td>SS</td>
<td>No reaction</td>
</tr>
<tr>
<td>Ta</td>
<td>No reaction</td>
</tr>
</tbody>
</table>

Figure 4.2 depicts the formation profile of the various phases formed in the reaction mixture with different sheath material powders during the in situ processing of MgB₂ heat treated at different temperatures. ‘Other phases’ labeled in the figure refers to all phases other than MgB₂ present in the samples and ‘reactive phase’ refers to compounds of sheath material with Mg and B. In all the cases formation of MgB₂ starts at 600 °C and the reaction rate attains a maximum in the temperature range from 675
Figure 4.2: Quantitative values of the various phases formed in the sheath material (a) Ag, (b) Cu, (c) Fe, (d) Ni, (e) SS and (f) Ta introduced in situ processed MgB$_2$ at different temperatures.

to 750 °C irrespective of the added sheath material powder. For Fe, SS and Ta the MgB$_2$ formation curves are almost identical (figure 4.2 c, e and
f) yielding high purity MgB$_2$ (Vol.% of 96.2, 97.2 and 96.1 respectively) at a temperature of 825 °C with little or no reacted phases. Beyond this temperature the rate of MgB$_2$ formation stagnates without any significant deterioration in purity upto 900 °C. But Ag, Cu and Ni added samples show (figure 4.2 a, b and d) markedly larger amount of reactive phases, considerably reducing the relative amount of MgB$_2$ phase in the core to 78.8%, 86.8% and 68.8% respectively within the temperature 900 °C. Of these, volume % of MgB$_2$ is lowest for the Ni added samples. The much higher reactivity of Ag, Cu and Ni make them unsuitable for the fabrication of MgB$_2$ based conductors even at lower temperatures.

![Figure 4.3: SEM images of the sheath material viz. Ag, Cu, Fe, Ni, SS and Ta added samples heat treated at 900 °C/2h.](image-url)
Figure 4.3 shows the scanning electron micrographs (SEM) of various sheath material introduced in situ processed MgB$_2$ samples heat treated at 900 °C/2h. Typical hexagonal grains of MgB$_2$ can be observed in all the microstructures. However, larger quantities of fine grained precipitates of the reacted products are observed for Ag, Cu and Ni added samples, showing their extensive reaction with Mg and/or B. In order to find out the atomic composition of the reacted phases energy dispersive X-ray (EDX) analysis was carried out. Figure 4.4 shows typical energy dispersive spectra (EDS) of the precipitated areas of Ag and Cu added in situ processed MgB$_2$ samples. The EDX microanalysis has revealed that the precipitated area of Ag added sample has an approximate atomic composition Mg : Ag of 1:1 (MgAg) and for Cu added sample, it has a composition Mg:Cu of 1:2 (MgCu$_2$). These observations are consistent with the X-ray diffraction studies.

![Energy dispersive spectra (EDS) of the reactive phase formed in Ag and Cu added samples heat treated at 900 °C/2h.](image)

For an in situ conductor fabrication method, the sheath material plays a very crucial role in determining the superconducting properties of MgB$_2$ conductors. Conductors with better properties could be achieved if we use the right sheath material which should be primarily non-reactive with Mg/B at heat treatment temperatures. The present study shows that Ag, Cu and Ni undergo markedly higher reaction during the in situ processing of MgB$_2$, which make them unsuitable for conductor fabrication. On the other hand, SS, Fe and Ta show no or very little reaction at the heat treatment temperatures and hence these can be considered as potential candidates for MgB$_2$ wire manufacturing. However, factors such as limited mechanical workability of SS and high cost of Ta make Fe, the best choice as the sheath material for in situ MgB$_2$ wire/tape fabrication.
4.2 Influence of sheath material reactivity on superconducting properties of MgB$_2$

4.2.1 Experimental Details

Based on the above study of the reactivity of various sheath materials with Mg/B, four samples, added with Fe, SS, Cu and Ni, (10 wt.% of each) and heat treated in air at 825 °C for 2 hours were selected for superconducting property measurements. Here after the samples added with SS, Fe, Cu and Ni are named as MBSS, MBFe, MBCu and MBNi respectively. The superconducting magnetic measurements were carried out by a vibrating sample magnetometer in Physical Property Measuring System (PPMS), Quantum Design, USA on the rectangular shape of samples having sizes of 3mm × 3mm × 1.5mm.

4.2.2 Results and discussions

The XRD patterns of the samples are shown in different plots in figure 4.1. However for the sake of comparison, the XRD patterns of samples added with SS, Fe, Cu and Ni sheath powders and heat treated at 825 °C for 2h are shown in figure 4.5. All X-ray diffraction results give sharp peaks of MgB$_2$ phase with only a minute fraction of MgO. The impurity phases formed are marked in the figure. Lattice parameter calculations show that there is no significant variation in lattice parameters $a$ or $c$ of MgB$_2$ (table 4.2) within the experimental limit. This indicates that the added sheath materials are not substituted at either Mg or B sites in MgB$_2$. The lattice parameters $a$ and $c$, Vol.% of MgB$_2$ phase, $T_C$, $H_{irr}$ and $J_C$ data for MBSS, MBFe, MBCu and MBNi samples obtained from this work are summarized in table 4.2.

Figure 4.6 illustrates the DC magnetization versus temperature (M-T) plots in zero field cooled (ZFC) condition under an applied field of 20 Oe for SS, Fe, Cu and Ni added MgB$_2$ samples. The ZFC branch of the magnetization undergoes a diamagnetic transition in the range 37.8-38.5 K. Fe added sample shows relatively higher $T_C$ (38.5 K) while $T_C$ of MBSS (38.2 K) and MBCu (38.3 K) are almost same and that of MBNi sample is slightly lower (37.8 K). The lower $T_C$ of Ni added sample may be due to the reduction of superconducting volume (60% MgB$_2$) which is cleared from quantitative phase analysis of XRD data, as shown in table 4.2. The samples MBSS and MBFe exhibit positive magnetization above transition.
4. Preparation and characterization of MgB$_2$ wires and tapes

![X-ray diffraction patterns for MgB$_2$ samples added with 10 wt.% of sheath powder SS, Fe, Cu and Ni and heat treated at 825 °C/2h.](image)

Temperature, likely due to the paramagnetic or ferromagnetic nature of additives. Although Ni is ferromagnetic below its Curie temperature, Ni added MgB$_2$ sample does not show any positive magnetization above $T_C$ since the Ni powder reacted with Mg and B forming MgNi$_{2.5}$Bi$_2$.

Table 4.2: Structural and superconducting characteristics of MgB$_2$ samples added with sheath materials. $J_C$ and $H_{irr}$ values are at 5 K

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>Vol. of MgB$_2$ (%)</th>
<th>$T_C$ (K)</th>
<th>$J_C$ at 2 T (A/cm$^2$) ($\times 10^4$)</th>
<th>$J_C$ at 5 T (A/cm$^2$) ($\times 10^3$)</th>
<th>$H_{irr}$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBFe</td>
<td>3.086</td>
<td>3.525</td>
<td>97.2</td>
<td>38.2</td>
<td>11.8 ($\times 10^4$)</td>
<td>6.8 ($\times 10^3$)</td>
<td>7.8</td>
</tr>
<tr>
<td>MBSS</td>
<td>3.089</td>
<td>3.523</td>
<td>96.2</td>
<td>38.5</td>
<td>8.5 ($\times 10^4$)</td>
<td>5.2 ($\times 10^3$)</td>
<td>7.7</td>
</tr>
<tr>
<td>MBCu</td>
<td>3.084</td>
<td>3.526</td>
<td>86.6</td>
<td>38.3</td>
<td>5.2 ($\times 10^4$)</td>
<td>2.9 ($\times 10^3$)</td>
<td>7.1</td>
</tr>
<tr>
<td>MBNi</td>
<td>3.086</td>
<td>3.525</td>
<td>60.0</td>
<td>37.8</td>
<td>4.5 ($\times 10^4$)</td>
<td>2.0 ($\times 10^3$)</td>
<td>6.9</td>
</tr>
</tbody>
</table>

The field dependent magnetization of MgB$_2$ samples added with sheath powders SS, Fe, Cu and Ni is shown in figure 4.7. It appears that the first
4. Preparation and characterization of MgB$_2$ wires and tapes

Figure 4.6: M-T plots in zero field cooled (ZFC) condition at 20 Oe for MBSS, MBFe, MBCu and MBNi.

and third quadrants and the second and fourth quadrants are replica to each other. The magnetic hysteresis loop widths of MBSS and MBFe are larger than those of MBNi and MBCu showing the former’s higher magnetization under external magnetic field. Samples MBFe and MBSS show slight paramagnetic shift due to the presence of paramagnetic components such as Fe and SS powders.

Figure 4.7: (a) M-H plots (at 5 K) of MgB$_2$ samples added with sheath powders SS, Fe, Cu and Ni and (b) enlarged view at high fields.
The critical current density \( J_C \) was estimated from the width of the M-H curves in applied fields \( (H) \) at 5 K by using Bean model. Figure 4.8 shows the dependence of \( J_C \) with magnetic fields upto 8 T. As shown in the figure \( J_C(H) \) characteristics imply that the intragrain \( J_C \) of Fe added MgB\(_2\) sample attains better values among all samples. The intragrain \( J_C \) values for MBFe sample are \( 11.9 \times 10^4 \) A/cm\(^2\) at 2 T and \( 6.8 \times 10^3 \) A/cm\(^2\) at 5 T whereas for MBSS sample \( J_C \) values at 2 T and 5 T are \( 8.5 \times 10^4 \) A/cm\(^2\) and \( 5.2 \times 10^3 \) A/cm\(^2\), comparable to that of Fe added sample. \( J_C \) values of sample MBCu are \( 5.2 \times 10^4 \) A/cm\(^2\) at 2 T and \( 2.9 \times 10^3 \) A/cm\(^2\) at 5 T and those of MBNi are \( 4.5 \times 10^4 \) A/cm\(^2\) at 2 T and \( 2 \times 10^3 \) A/cm\(^2\) at 5 T. Enhanced \( J_C \) values of Fe and SS added samples show a direct correlation with their better phase purity comparing with Cu and Ni added samples. At higher fields MBSS and MBFe samples show two or three times larger \( J_C \) than the other samples containing reacted phases. The steep drop in \( J_C \) at higher fields (> 6 T) in all samples is attributed to the flux penetration into the grain boundaries that may contain impurities. The weaker grain connectivity and greater flux penetration due to the presence of impurities of reacted sheath powders in the grain boundaries lead to a larger reduction of \( J_C \) in MBCu and MBNi samples at higher fields.
The irreversibility field $H_{\text{irr}}$, defined as the field at which critical current $J_C$ falls below 100 A/cm$^2$, for all samples at 5 K is shown in table 4.2. For MBFe and MBSS $H_{\text{irr}}$ values at 5 K are 7.8 T and 7.7 T while those of MBCu and MBNi are 7.1 T and 6.9 T respectively. Higher $H_{\text{irr}}$ of Fe and SS added samples is attributed to the higher superconducting area, better microstructure and unreacted sheath powders in MgB$_2$ acting as grain boundary pinning centers. The reacted additives in Cu and Ni added samples reduce the superconducting area and weaken the grain connectivity without any enhancement in flux pinning, causing reduced $J_C(H)$ and $H_{\text{irr}}$ values.

From the results it is very clear that Fe is the most suitable material with respect to chemical inertness with Mg/B at the reaction temperature and retention of superconducting properties of the MgB$_2$ core. Fe is easily available and is relatively cheap. It has adequate hardness to give mechanical support to the brittle superconducting core. It has enough strength and ductility to withstand mechanical rolling. Fe sheath effectively acts as a diffusion barrier for the volatile and reactive Mg. Considering these facts we choose iron as the sheath material for MgB$_2$ conductor fabrication.

4.3 Preparation of MgB$_2$ conductors

Mono and multifilamentary MgB$_2$ wires and tapes were prepared by the \textit{in situ} Powder-In-Tube (PIT) method. Figure 4.9 presents the preparation method of mono and multifilamentary MgB$_2$ wires and tapes.

4.3.1 Monofilamentary wires and tapes

Fe tubes of length 2.5-5 cm, outside diameter 4 mm and inside diameter 2 mm were used for the regular short length conductor fabrication. For long length conductors 5-10 cm long and OD/ID of 8/6 or 5/3 mm tubes were used. The tubes were filled with homogeneously mixed Mg and B powders and mechanically compacted. Brass studs were used as plugs to seal the ends of the tubes. The composite tubes were groove rolled down to desired dimensions without any intermediate annealing. The regular wires prepared had a diameter of 1.4-2.0 mm, while the minimum diameter for rolled wire was $\sim$ 1.1 mm. For the preparation of tapes these groove rolled wires were then flat rolled to the desired geometry, using a flat roller. Typical flat rolled tapes had dimensions $3-4 \times 0.8-1.6$ mm (width $\times$ thickness).
The ends of the wires and tapes were sealed by arc welding. These wires and tapes were then heat treated at 650-750 °C for 0.5-2 hours. Some of the wires/tapes were heat treated by electrical self-heating (described in section: 4.8) and others were heat treated in a muffle furnace. After heat treatment short length samples were cut for various characterizations.

Figure 4.9: Flowsheet showing the preparation method of mono and multifilamentary MgB₂ wires and tapes.

4.3.2 Multifilamentary wires and tapes

In a stabilized practical multifilamentary conductor, there has to be many filaments of sheathed MgB₂ superconductor in a metallic matrix. A signifi-
4. Preparation and characterization of MgB$_2$ wires and tapes

Cant area fraction of the multifilamentary conductor must contain a thermal stabilizer material: metals with high thermal and electrical conductivities. During an accidental quench the stabilizer has to dissipate the heat generated in the conductor as fast as possible. The stabilizer also provides a parallel path to the current flow during the quench. In the present work we prepared multifilamentary MgB$_2$ conductors using Fe as inner sheath, Cu as stabilizer and Ni as outer sheath. Cu is used as the stabilizer, since it has high thermal and electrical conductivity and relatively low cost.$^1$ The outer sheath must have good mechanical properties to support the conductor and must be chemically stable with environment. We have considered stainless steel (SS), mild steel (MS), monel (an alloy of Cu and Ni) and Ni for the outer sheath material. Among these Ni is chosen as the outer sheath due to its high oxidation resistance at high temperature heat treatment and good mechanical properties.

To prepare multifilamentary wires the grove rolled monofilamentary wires (OD $\sim$ 2-2.5 mm) were cut, bundled and packed inside Ni tubes of outside diameter 8 mm and inside diameter 6 mm. Cu wires of diameter 0.75-2 mm were also bundled inside the Ni tube along with the filaments. The composite was then then groove rolled for multifilamentary wires. For the preparation of tapes these groove rolled wires were then flat rolled to the desired geometry. The rolled wires and tapes were then heat treated as in the case of monofilamentary ones. The maximum length of the wire prepared is about 2 m and the maximum number of filaments in multifilamentary wires is 10. A typical wire has 1.5-2 mm outside diameter and a typical stabilized tape has the dimensions of $\sim$ 1-2 mm thickness and 3-5 mm width and upto 10 superconducting filaments.

Figure 4.10 shows a schematic diagram of the filling and rolling processes for both mono and multifilamentary conductors and for both wire (groove rolling) and tape (flat rolling) rolling. For the rest of the thesis, the following short names are used to represent mono and multi filamentary wire and tape samples.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Short Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono (Single) filamentary Wire</td>
<td>SW</td>
</tr>
<tr>
<td>Mono (Single) filamentary Tape</td>
<td>ST</td>
</tr>
<tr>
<td>Multi filamentary Wire</td>
<td>MW</td>
</tr>
<tr>
<td>Multi filamentary Tape</td>
<td>MT</td>
</tr>
</tbody>
</table>

$^1$Silver (Ag) also has high thermal and electrical conductivity, but it is expensive.
4. Preparation and characterization of MgB$_2$ wires and tapes

4.4 Problems faced during fabrication of conductors

Compared to the MgB$_2$ bulk preparation, the wire and tape preparations were faced with a number of problems. The major problem faced during fabrication was the cracking of the sheath material. Even micro cracks proved costly because MgO content of such samples was very high which seriously affected the superconducting property. Figure 4.11 (a) shows a piece of wire which cracked during rolling. Figure 4.11 (b) shows the same region after the heat treatment. Here the crack is further developed and the MgO formed is seen as a white cloudy mass. For wires and tapes the surface cracking during rolling arises mainly due to work hardening and/or sheath thinning. By selecting tubes with proper wall thickness, optimizing the initial powder packing density and controlling the area reduction rate during rolling etc we could solve the sheath cracking problem completely. For wires, in addition to the surface cracking, there was edge cracking also. This generally occurred during initial stages of flat rolling, where the cross section of the conductor starts to change from circular to rectangular. This problem also was solved by controlling the rolling parameters such as rolling speed and area reduction ratio per pass etc. For both wires and tapes the cracking tendency was higher for multifilamentary geometries. The problem of cracking was more in lower grooves.

In the case of multifilamentary conductors the ductility mismatch between Fe, Cu and Ni also caused rolling problems. These materials elongate differently during the initial stages of rolling. The initial non uniform
4. Preparation and characterization of MgB$_2$ wires and tapes

Figure 4.11: Photograph of (a) a macro scale crack on the surface of a rolled mono wire and (b) the same region after heat treatment (The photograph is taken on electrically self-heated sample). Here the crack is further developed and the MgO formed is seen as a white cloudy mass.

elongation results non uniform properties at both the ends, compared to the middle of the conductor. As the rolling progresses the diameter of the composite tube gets reduced and the whole composite elongates together. In order to account this, a portion of both ends of the rolled conductors were cut before heat treatment. The end sealing of conductors before heat treatment also raised some hurdles. Fe is easily weldable while Ni and Cu are not. A capping technique is used to perfectly seal the ends. In this, the ends of the conductors were inserted to suitable iron tubes of short length and mechanically fixed with the conductor and then ends of the iron tubes were welded. Figure 4.12 shows schematic illustrations of the problems as described above.

Figure 4.12: Schematic Illustrations of some of the problems faced during rolling.
4. Preparation and characterization of MgB$_2$ wires and tapes

Figure 4.13: SEI SEM images of cross sections of (a) mono wire, (b) mono tape and (c) the core of mono wire.

4.5 Structural characteristics of MgB$_2$ conductors

Figure 4.13 shows the SEI SEM images of a mono filamentary wire (a) and tape (b). The images also show distinct and clear sheath and core as observed in the optical micrographs. Figure 4.13 (c) shows the enlarged view of the core of the wire. The image shows large pores in the core, characteristics of \textit{in situ} synthesized MgB$_2$, caused due to the low green

Figure 4.14: Optical micro graphs of multifilamentary MgB$_2$ conductors (a) 4 filament wire (b) 8 filament wire and (c) 4 filament tape. Dimensions : OD = 2.1 mm for wires and cross section = 4 × 1 mm$^2$ for tape.
density of the mixtures and the volume shrinkage during MgB$_2$ formation.

Figure 4.14 shows the optical micrographs of the cross sections of some of the monofilamentary and multi filamentary samples. The micrographs show the MgB$_2$ core distinct and clear in both mono and multi. The outer sheath, superconducting core and the metallic matrix are clearly visible and distinguishable. The core-sheath interface is observed to be distinct, indicating the non-reactivity of the core with sheath metal. The Cu wires are also clearly visible without any significant diffusion between the different metals. No cracks or non uniformities were observed and the cross section of the wire and tape are almost circular and rectangular respectively in the micrographs.

Optical microscopy measurements, taken with the help of a scale built into the eyepiece, were used for the exact estimation of core and sheath cross sectional areas of mono/multi filamentary wires/tapes. For both mono wires and tapes, MgB$_2$ core has $\sim 25\%$ and the Fe sheath has $\sim 75\%$ of the total cross sectional area respectively. The relative cross sectional area of MgB$_2$ core for mono filamentary wire and tapes are shown in figure 4.15. For a typical multifilamentary conductor the cross sectional area $\sim 10\%$ for MgB$_2$ core, $\sim 8\%$ for Cu, $\sim 35\%$ for Fe and $\sim 47\%$ for the outer Ni sheath.

![Graph]

Figure 4.15: The cross sectional area of MgB$_2$ core (in percentage) for mono filamentary wires and tapes for different diameter and thickness.

The powder XRD pattern of the ground MgB$_2$ core of a monofilamentary wire is shown in figure 4.16, as a typical case. Crystalline MgB$_2$ with minor amounts of MgO is observed in the samples. Unlike some of
the earlier reports no peaks of Fe containing phases such as Fe\(_x\)B phases are observed in the samples. This shows the non-reactivity of the sheath material with the Mg/B powders at the reaction temperature. The quality (crystallinity and phase purity) of MgB\(_2\) formed in the wire/tape is as good as that of MgB\(_2\) bulks prepared by PIST method as discussed in chapter 3. Calculated lattice parameters of the prepared MgB\(_2\) wires and tapes were consistent with the values observed for bulks.

![Peaks of MgB\(_2\) are indexed](image)

Figure 4.16: Powder XRD pattern of the ground MgB\(_2\) core of a monofilamentary wire.

### 4.6 Superconducting properties of MgB\(_2\) conductors

Figure 4.17 and 4.18 show the resistance versus temperature plots of a mono and multifilamentary wire and tape samples. Inset of the figures show the enlarged plots near the transition region. Both mono and multi wire and tape have sharp transition at around 39 K. Mono filamentary conductors have a transition temperature (\(T_C\)) in the range 38.2-39.0 K with transition width \(\Delta T_C < 1\) K. For multi filamentary conductors the \(T_C\) was in the range 38.0-38.5 K with transition width \(\Delta T_C < 1.5\) K. The almost
4. Preparation and characterization of MgB$_2$ wires and tapes

Figure 4.17: R-T plots of typical monofilamentary wire and tape. Inset of the figure shows zoomed view near the superconducting transition.

constant $T_C$ and low $\Delta T_C$ values of the wires/tapes as those observed in bulk samples indicate the good quality and homogeneity of the superconducting core in the wire/tape.

Figure 4.18: R-T plots of typical multifilamentary wire and tape. Inset of the figure shows zoomed view near the superconducting transition.
Another important task is to find the current carrying capability of the prepared conductors. The measurement of transport current properties of MgB$_2$ conductor is difficult especially at high currents (in self-field). The rapid warming of the current contacts may cause a premature quench and subsequent burn out of the sample. In cases when very high currents are passed the contact, especially the solder joints melts. Figure 4.19 shows the photograph of such a sample where the contact is broken. The current contact melted while passing $\sim$ 870 A current through the sample (monofilamentary wire of OD $\sim$ 1.33 mm, length 3 cm) at 4.2 K and self-field. In the present study I-V measurements (cryocooler based) were done at relatively high temperatures to restrict the current to low values, other
wise the heat generated at the current leads and contacts make the transport measurements difficult in the conduction cooling system.\(^2\)

Figure 4.20 shows the I-V characteristics of a monofilamentary MgB\(_2\) wire at different temperatures. The sample had a length of 6.5 cm and \(\sim 1.33\) mm diameter. The wire had a MgB\(_2\) core of \(\sim 0.68\) diameter. The sample was heat treated at 650 °C for 1 hour. The I-V measurement is done at 28, 30, 31 and 32 K using a closed cycle cryostat, where the sample is cooled by conduction. Current is passed through the sample for few seconds and the corresponding voltage drop across a tap of gap 2 cm is noted and then the current was switched off for few seconds to remove the heat generated in the current leads. The wire showed a critical current of \(\sim 91\) A at 28 K, 85 A at 30 K, 75 A at 31 K and 56 A at 32 K respectively. Table 4.3 shows the corresponding critical current density and engineering current density for the sample. The sample have a engineering current density of more than \(10^3\) Acm\(^{-2}\) and critical current density of more than \(10^4\) Acm\(^{-2}\) at a temperature around 30 K.

Table 4.3: Critical current characteristics of the sample for the I-V plot shown in figure 4.20

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(I_C) (A)</th>
<th>(J_E) ((\times 10^3) Acm(^{-2}))</th>
<th>(J_C) ((\times 10^4) Acm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>91</td>
<td>6.5</td>
<td>2.5</td>
</tr>
<tr>
<td>30</td>
<td>85</td>
<td>6.1</td>
<td>2.3</td>
</tr>
<tr>
<td>31</td>
<td>75</td>
<td>5.4</td>
<td>2.1</td>
</tr>
<tr>
<td>32</td>
<td>57</td>
<td>4.0</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Figure 4.21 shows the I-V characteristics of selected multi filamentary wires and tapes at 30 K. The corresponding engineering and critical current densities are tabulated in the inset of the figure. The wires have 1.6 mm diameter and 5 (for MW1) and 8 (for MW2) superconducting filaments. The tapes measured have cross sections 3.2 \(\times\) 1.0 and 2.6 \(\times\) 1.1 (in mm)

\(^2\)During the undesirable quench the measured parameters may not be the intrinsic property of the conductor. It has also been suggested that some of the high \(n\) (sharp transitions) values measured arise due to the heating during the I-V measurement, rather than the intrinsic value [170]. In order to avoid these difficulties it is a general practice to measure the transport properties at relatively higher temperatures or higher applied fields [171–174].
and 4 superconducting filaments. Sample MW1 has a sharp transition at around 96 A, while the 8 filament multifilamentary wire of same OD has a less sharp transition at around 80 A. The tape samples have relatively lower $I_C$ and $J_C$ values compared to the wire samples.

**Figure 4.21:** I-V plot of typical multifilamentary MgB$_2$ conductors at 30 K.

### 4.7 Continuous current characteristics of multifilamentary MgB$_2$ conductors (In helium vapour)

In the present work transport current measurements of the MgB$_2$ conductors were done using a closed cycle cryocooler based cryostat or in a liquid helium cryostat. In the cryocooler based measurements the sample was in a vacuum chamber and was cooled by conduction. In the liquid helium dewar or cryostat, the sample was in liquid or vapor helium and was cooled by the direct contact with liquid or vapor helium. In the cryocooler measurements transport currents were passed for short durations only, while in
the liquid helium cryostat measurements the transport currents were passed continuously, with different ramp rates. This section describes the results and analysis of continuous transport current measurements done in liquid helium cryostat. All the measurements were done at the superconductor and magnet division, Institute of Plasma Research (IPR), Gandhinagar.

Figure 4.22: (a) I-V plot of a multifilamentary wire at different temperatures, (b) the variation of critical current with temperature and (c) I-V plot for different current ramp rates.

Figure 4.22 (a) shows the I-V plots of a multifilamentary wire at different temperatures. Figure 4.22 (b) shows the plot of critical current ($I_C$) versus temperature for the sample. The measurements were done with current ramp rate of $\sim 1$ A/S. The sample measured had an outer diameter of $\sim 2.0$ mm, length of 10.5 cm. The voltage taps were soldered in the middle of the sample with a gap of 6.5 cm between them. The sample shows relatively sharp transition at lower temperatures, but the transition is less sharp or slightly broadened at higher temperatures. In the I-V plot at 6.7 K, the voltage across the voltage tap increases sharply above 151 A. And thus 151 A is taken as the $I_C$ of the sample at 6.7 K. The sample has $I_C$ of 151 A at 6.7 K, while at 23.6 K the value of $I_C$ is decreased to 68 A. The value of $I_C$ of the sample decreases almost linearly with the temperature.

In all the I-V plots, before the sharp rise in the voltage (for currents below $I_C$) a current depended linear background voltage is observed. This background voltage observed is due to the current transfer problem [pages 307-317 of ref: 175]. In principle, for currents far below the critical current
the voltage should be close to zero. This background voltage observed in
the samples is due to the current sharing problem between the supercon-
ducting filaments and the metallic materials (sheath, matrix and stabilizer),
and the problem of current transfer needs special attention for the develop-
ment of MgB$_2$ conductor.

In a sheathed conductor, the transport current has to pass through the
contact materials (current lead and solder) and also through the metallic
sheath before entering into the superconducting core. The penetration of
current from the outer core to the superconducting core happens over a
length, depending on the nature of the sheath material and the interface
between the sheath and superconductor [176, 177, and pages 306, 307 of
ref:14]. such a current transfer is accompanied by additional voltage close
to the current contact [178, 179].

Figure 4.22 (c) shows the I-V characteristics of the wire measured with
different current ramp rates at 6.7 K. The background voltage observed is
independent of the current ramp rate at all the temperatures. But the onset
of sharp rise in voltage ($I_C$) shows some dependence with the current ramp
rate. In general the value of $I_C$ is slightly higher for measurements done
with higher current ramp rate. This is behavior is observed for measure-
ments done at other temperatures also.

Two more multifilamentary samples (one wire and one tape) were mea-
sured for analyzing the transition details. The details of samples are given
in table 4.4. The samples used had four MgB$_2$ filaments and voltages from

3In a straightforward model of a joint between a metal lead and a superconductor the
current in the lead decays exponentially [179, 180] and the current transfer length is approx-
imated as the ratio between the transverse matrix to filament resistance and the longitudinal
matrix resistance. So that

$$\lambda = \sqrt{\frac{R_b \times t_n}{\rho_n}}$$

where $R_b$ is the resistance per unit area of the matrix-superconductor interface and $t_n$ is the
interface thickness and $\rho_n$ is the longitudinal resistivity of the matrix (sheath). From this
equation it is clear that the current transfer length increases with interface resistance and its
thickness, which are much higher in the case of multifilamentary conductors. For a typical Fe
sheathed mono filamentary MgB$_2$ conductor the current transfer length will be several (1-4)
nilli meters [178, 179]. For a multifilamentary conductor (as studied here) there are materials
with different resistivities and different interfaces, making the current transfer from the outer
sheath to the superconductor much more complex.
two sets of taps from each sample were monitored for studying the nature of transition.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Geometry</th>
<th>Cross sectional dimensions</th>
<th>Length (cm)</th>
<th>Distance (cm) between voltage taps Tap 1</th>
<th>Tap 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW wire</td>
<td>$\phi = 2.1$ mm</td>
<td>10.5</td>
<td>6.0</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>MT tape</td>
<td>$3.0 \times 1.2 \text{ mm}^2$</td>
<td>7.5</td>
<td>3.7</td>
<td>7.0</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.23 shows the I-V characteristics of the MW and MT samples, at 15 and 21 K, respectively. Figure 4.23 (a) shows the I-V plots in linear scale and, while figure 4.23 (b) shows the same with the y axis (Voltage) in log scale. For both the samples current is charged at $\sim 1$ A/s. The sample MW shows a sharp transition at 208.4 A (at 15 K). The transition point is same (208.4 A) for both the voltage taps having gap 6 and 10 cm, and the voltage rises sharply for both the taps above the transition. The similar response in both the voltage taps indicates good superconducting homogeneity along the length of the sample. For the tape sample the transition is less sharp compared to the wire. The transition (voltage rise) started at around 110 A in both the voltage taps and the slope of the curve changed significantly around 150 A.

Figure 4.23: I-V plot of samples MW and MT in(a) linear-linear and (b) log-linear scales.

The log scale plot given in figure 4.23 (b) clearly shows the current depended voltage below the sharp rise in voltage. The values of background
voltage were more in tap 2 for both the wire and tape samples. This is expected as the tap 2 has large gap between them and are close to the current contacts than tap 1. So that the current transfer interfered with these readings. The background voltage is more for the tape sample.

![Figure 4.24](image)

**Figure 4.24:** Transport current, voltage across taps and the sample temperature during the measurement, for (a) wire and (b) tape sample. Legends are I:Current, V1: Voltage at tap 1, V2: Voltage at tap 2 and T: Temperature.

Figures 4.24 (a) and (b) show the transport current, voltage across the two voltage taps on the sample and the sample temperature during the measurement for the wire and tape samples respectively. The current values are shown in multiples of hundred for clear visibility. For both the wire and tape the two figures show identical behavior (except the values of the parameters). Considering the plot of wire sample, the sample showed an $I_C$ of 208.4 A as shown in I-V plots. At this value of current the voltage across of both the taps raised sharply. The current sources voltage (not shown here) also rose suddenly for this current and as the power supply voltage reached a preset value (8 V in this case) the current is cut off automatically. Consequently the voltages across the two taps decreased.

The temperature of sample was 15 K at the start of current charging and the temperature linearly increased with current upto $\sim 208$ A. At this current the sample temperature was 16 K, 1 K above the starting temperature. This increase in temperature is due to the current sharing with resistive matrix and insufficient thermal stability of the composite conductor. The current passing through the normal resistive layers near the current contacts (within the CTL) generates heat. This heat generation at the ends of the composite can cause undesirable quenching of the superconductor at
transport currents much lower than the current it can actually carry. In the present case, at the onset of transition (around 208 A) the sample temperature is 16 K and then there is sudden increase of temperature by $\sim$ 2 K. The sample showed increased temperature even after the current is turned off and the temperature settled at 4 K above the temperature before transition. This shows the sudden quenching and rapid warming of the sample at around the current of 208.4 A.

For the tape sample the rise of temperature was even higher. During the quenching the temperature of the increased from 21 K to 42 K! This is above the transition temperature of MgB$_2$. One thing here to suspect is whether the observed $I_C$ is a true critical current of the sample or a reduced one due to the temperature increase (insufficient cryostability). These results clearly shows the insufficient thermal stability of the prepared multifilamentary MgB$_2$ conductors. For the practical use of multifilamentary MgB$_2$ conductors the thermal stability has to be ensured and there is a great need for further research to address this issue. As observed earlier for the above wire and tape samples the relative area of MgB$_2$ core is $\sim$ 10% and the area of Cu thermal stabilizer is $\sim$ 8%. The low thermally and electrically conducting Fe and Ni occupy a significant percentage of the area of the crosssection ($\sim$ 82%). This is the reason for the insufficient thermal stability of the conductures. Future research must be focussed on increasing the Cu and MgB$_2$ area fraction without sacrifising the strength and quality of the conductor.

### 4.8 Preparation and characterization of MgB$_2$ conductors by electrical self-heating

In the electrical self-heating method sheathed MgB$_2$ conductors were prepared by heating the conductor using electric current (either DC or AC), instead of the regular furnace heating. For the electrical self-heating method, mono filamentary wires/tapes were rolled as described in section 4.3. These fabricated wires were then subjected to electrical self-heating by employing a DC current source (Voltage : 0-20 V, Current : 0-30 A).

#### 4.8.1 Experimental details

For a typical sample preparation wire sample of length about 50 cm was held horizontally through the axis of a tubular thermal insulator (inside
diameter: 2.5 cm) fabricated from alumina fiber board and the ends of the sample were connected to the current source through a programmable temperature controller, a thermocouple which was kept at the middle of the sample to monitor the temperature. The sample was heated by passing a suitable current through the sample, either manually or automatically through a PC interface. A schematic diagram of the set up used for electrical self-heating is shown in figure 4.25. Figure 4.26 shows the photograph of the set up used to electrically self-heat samples of length 10-30 cm in air. The thermal insulation is removed for clear visibility of the sample.

Figure 4.25: Schematic diagram of the preparation of MgB$_2$ conductors by electrical self-heating method.

Figure 4.26: Photograph of electrical self-heating of a MgB$_2$ conductor.
4.8.2 Results and discussion

The results of two monofilamentary wire samples, SW1 with OD = 1.1 mm and length = 40 cm and SW2 with OD = 1.6 mm and length = 25 cm are discussed here. For both the samples the Fe sheath to MgB₂ area fraction is around 80:20. The sample SW1 was heated at 750 °C for 15 minutes and SW2 was heated at 700 °C for 30 minutes. The figure 4.27 shows power schedule for sample preparation for the two typical cases. For SW1 the energy required for one typical experiment is estimated to be about 60 Whr only, of which about 30 Whr (7 V × 17 A × 0.25 hr) is used for soaking for 15 minutes and 30 Whr is used for controlled heating and cooling. The time required for one experiment is typically 45 minutes. For SW2, the total energy required is about 70 Whr, of which ∼ 45 Whr is used for soaking at 700 °C for 30 minutes and the remaining 25 Whr is equally shared for heating and cooling. The total time taken for SW2 is one hour. Evidently, the ESH method is highly energy efficient since the electric power is used only for heating the sample alone.

![Figure 4.27: Power schedule for typical electrical self-heating experiments.](image)

Figure 4.28 shows the XRD patterns of the wire samples SW1 and SW2 prepared by electrical self-heating method. The XRD patterns reveal that almost phase pure MgB₂ is formed in the samples with very sharp and
strong peaks comparable to that observed in furnace heat treated wire/tape samples. No peaks of Fe$_x$B phases are observed here also suggesting that the sintering temperature used here is suitable for the formation of MgB$_2$ wires with little or no reaction between Fe and the superconductor matrix. Calculated lattice parameters of the prepared MgB$_2$ were obtained as $a = 3.086 \pm 0.002$ Å and $c = 3.524 \pm 0.001$ Å, which are consistent with values observed for bulks and other furnace heat treated conductors.

![XRD spectra of the core of samples prepared by electrical self-heating method.](image)

Figure 4.28: XRD spectra of the core of samples prepared by electrical self-heating method.

The $T_C$ of the samples from R-T measurements were found to be 37.90 K and 38.45 K for SW1 and SW2 respectively. The I-V plots at 25 K for the samples are also shown in figure 4.29. The sample SW1 has a relatively low $I_C$ due to its smaller cross section. These transport properties are comparable to those of samples prepared with furnace heat treatment. Thus it is demonstrated for the first time that good quality MgB$_2$ conductors can be prepared by a simple and energy efficient electrical self-heating method.

The electrical self-heating produces good quality MgB$_2$ conductors with crystalline and superconducting properties as good as those of furnace heat treated samples. Most of the electrical self-heating synthesis are done with DC power source. However since AC power source is cheaper the use of AC source is also carried out and the results are found to be identical as that of DC power source.
4. Preparation and characterization of MgB$_2$ wires and tapes

The electrical self-heating method has many advantages such as less power consumption, short preparation time, less preparation cost due to the avoidance of special furnaces with inert gas atmosphere. The method is highly suitable for processes wherein rapid heating or cooling is essential. It is possible to translate the method into a continuous hot rolling process with an array of groove rollers initially for wire making followed by a pair of rollers at the end to which electrical power can be supplied directly. Thus from an industrial point of view the present method is more economical and easy for continuous production of sheathed MgB$_2$ conductors.

4.9 Summary and conclusions

A systematic study on the chemical computability of different sheath materials with Mg/B is conducted and based on the results of the study, Fe is selected as a suitable sheath material for the MgB$_2$ wire and tape preparation. Fe sheathed MgB$_2$ wires tapes were prepared by in situ Powder-In-Tube method in mono and multifilamentary geometries. The prepared multifilamentary wires were characterized for phase purity and superconducting properties. The prepared multifilamentary conductors have good transport current carrying, comparable to the internationally reported for
MgB₂ conductors. A simple and energy efficient electrical self-heating method is introduced for the preparation of MgB₂ conductors.