5.1: Introduction

Impressive progress has been made in the fabrication of MgB$_2$ wires for practical applications such as magnets and cables, since its discovery. The key to magnet applications of superconductors lies in the rare combination of low cost and a ready wire fabrication route. Due to the recent advances in cryocoolers, many electric utilities have to be optimized at temperatures of 10-35 K, a domain for which MgB$_2$ could provide the cheapest superconducting wires. Another important advantage of the MgB$_2$ conductor fabrication compared to the other superconductors is that the formation of MgB$_2$ phase with better superconducting properties occurs at relatively low temperatures and short durations. The first successful process of MgB$_2$ wire fabrication, via diffusion of Mg vapor into boron fibers encapsulated in Ta tubes, was reported by Canfield et al. [1]. Soon after, many techniques were developed to produce long wires with higher critical current densities ($J_C$). Among these, powder in tube (PIT) method came out as the most acceptable method for preparation of good quality wires in long length. Based on this method, certain groups [2-4] followed the so called ex situ technique, while majority [5-8] preferred to use the in situ technique. Though ex situ technique is found to be suitable for the development of long conductors with complex multifilamentary wire geometry, the $J_C(H)$ behavior of the ex situ conductors has not been as good as the in situ ones. Besides this, in situ route has several advantages such as low cost, low processing temperature and easiness to dope impurity atoms at Mg/B sites. However, the superconducting properties of in situ PIT processed MgB$_2$ wires strongly depend on the type and quality of precursor powder, chemical compatibility and workability of sheath material, processing temperature and preparation techniques. Therefore, the reactivity of sheath materials with Mg/B, effects of processing temperature, substitution and
addition of impurity atoms and nano dopants and novel preparation techniques such as lowering the processing temperature of MgB$_2$ and hot-pressing of self-heated MgB$_2$ wires are studied in detail and discussed in this chapter.

5.2: Influence of reactivity of sheath materials with Mg/B on superconducting properties of MgB$_2$

5.2.1: Introduction

On considering the fabrication of metal sheathed MgB$_2$ conductors, the metal sheath should play the role of a diffusion barrier for the volatile and reactive Mg and it must be chemically compatible with Mg/B without any degradation of superconducting properties of MgB$_2$ core. Moreover, the sheath material must have adequate strength to give mechanical support to the brittle superconducting core and should be ductile enough to withstand the mechanical working. A number of sheath materials viz. Fe, Ni, Cu, Ag, Nb, Ta and SS have been used to fabricate MgB$_2$ wires [9-16]. Among these, most of them form intermetallics or solid solutions with Mg/B causing reduction in superconducting volume and critical current. Apart from sheath reactivity, sheath materials such as Ag, Nb and Ta are very much expensive. Hence, the effect of the reactivity of commonly used sheath materials such as Cu, Ni, Fe and SS on superconducting properties of MgB$_2$ was investigated to understand the chemical compatibility of these sheath materials for preparation of MgB$_2$ wires.

The samples were prepared by in situ PIST method as detailed in the previous chapters. Stoichiometrically weighed Mg, amorphous B and 10 wt% of sheath material powder (Cu, Ni, Fe and SS of size <75 µm) were uniformly mixed, then packed into the SS tubes and heat treated at different temperatures. SS tube was chosen as the sheath material because of its relatively better chemical stability and mechanical strength at elevated temperatures. The XRD analysis of the above mentioned samples processed at different temperatures showed better result at 825 °C and hence the samples processed at this temperature were chosen for further superconducting measurements. The samples added with Cu, Ni, Fe and SS are labeled as MBCu, MBNi, MBFe and MBSS respectively.
5.2.2: Results and discussion

The results obtained from XRD analysis of MgB₂ added with the powders of various sheath materials processed at different temperatures are summarized in table 5.1. ‘Pure’ phase corresponds to MgB₂ and ‘others’ corresponds to Mg and MgO for all samples, while ‘reacted’ phase corresponds to Mg₂Cu/MgCu₂, MgNi₂.₃B₂ and FeB₂ for MBCu, MBNi and MBFe samples respectively. Semi quantitative phase analysis of the samples was done from XRD data using the formula, Vol% of phase \( X = \left( \frac{\Sigma I_X}{\Sigma I} \right) \times 100 \) where \( \Sigma I_X \) = sum of integrated peak intensities of phase X and \( \Sigma I \) = sum of integrated peak intensities of all phases and the data are given in table 5.1 for comparison.

Table 5.1: Volume percentage of various phases formed at different processing temperatures for MgB₂ samples added with Cu, Ni, Fe and SS

<table>
<thead>
<tr>
<th>Samples</th>
<th>Phases</th>
<th>Vol.% of various phases</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>600 °C</td>
</tr>
<tr>
<td>MBCu</td>
<td>Pure</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>Reacted</td>
<td>39.9</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>57.6</td>
</tr>
<tr>
<td>MBNi</td>
<td>Pure</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>Reacted</td>
<td>45.3</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>52.5</td>
</tr>
<tr>
<td>MBFe</td>
<td>Pure</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>Reacted</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>93.5</td>
</tr>
<tr>
<td>MBSS</td>
<td>Pure</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>Reacted</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>96.7</td>
</tr>
</tbody>
</table>

In MBCu sample, Mg and Cu reacts even at 600 °C leading to the formation of a binary phase Mg₂Cu. As the reaction temperature is increased to 750 °C, Mg₂Cu undergoes partial decomposition and releases a part of the Mg resulting in the phase formation of MgCu₂. These reactive phases both Mg₂Cu and MgCu₂ reduce the volume of MgB₂ considerably as shown in table 5.1. MBNi also shows significant reaction at temperatures as
low as 600 °C causing the formation of Mg$_2$Ni similar to MBCu samples. At higher temperatures, B also takes part in the reaction process resulting in the formation of a tertiary compound MgNi$_{2.5}$B$_2$. The rate of this reaction is very fast and hence the reaction consumes significant parts of Mg and B leading to an increase in porosity of the superconducting core and thus lowering the superconducting properties. Thus, both Ni and Cu show distinct reactions with Mg/B even at 600 °C and reduce the amount of MgB$_2$ noticeably which make them unsuitable for conductor fabrications.

In the case of MBFe, Fe remains inert towards both Mg and B at temperatures up to 825 °C. But an intermetallic compound FeB$_2$ begins to form at around 900 °C due to the reaction of Fe with B. Mg and B are found to be inert in MBSS samples even up to the highest heat treatment temperature of 900 °C, and it may be recalled that SS tubes were used for preparing all the samples in this study. Not even a trace of any reacted phase associated to SS is observed in any of the samples under the extreme heat treatment conditions used. Thus it is confirmed that Fe and SS do not react with Mg or B even up to 825 °C where phase formation of MgB$_2$ almost completes, suggesting the chemical compatibility of Fe and SS for MgB$_2$ wire fabrication. Hence, the samples processed at 825 °C were chosen for further detailed investigation.

![XRD patterns of MgB$_2$ samples added with Cu, Ni, Fe and SS powders processed at 825 °C](image)

Figure 5.1: XRD patterns of MgB$_2$ samples added with Cu, Ni, Fe and SS powders processed at 825 °C
Figure 5.1 shows the XRD patterns of samples added with SS, Fe, Cu and Ni sheath powders processed at 825 °C. All X-ray diffraction results give sharp peaks of MgB$_2$ phase with only a minute fraction of MgO. Absence of any reacted phases of Fe and SS with Mg/B in MBFe and MBSS samples shows their chemical compatibility for wire fabrication, whereas significant quantities of reacted phases such as MgCu$_2$ and MgNi$_{2.5}$B$_2$ are present in MBCu and MBNi respectively. Lattice parameter calculations show that there is no significant variation in lattice parameters of MgB$_2$ (table 5.2). This indicates that the added sheath materials are not substituted at either Mg or B sites in MgB$_2$. For the sake of comparison, the lattice parameters, $T_C$ and $J_C$ data for MBCu, MBNi, MBFe and MBSS samples are summarized in table 5.2.

Table 5.2: Lattice parameters, $T_C$ and $J_C$ of MgB$_2$ added with various sheath materials

<table>
<thead>
<tr>
<th>Samples</th>
<th>Lattice parameters(nm)</th>
<th>$T_C$ (K)</th>
<th>$J_C$ at 5 K (A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>4 T ($\times 10^4$)</td>
</tr>
<tr>
<td>MBCu</td>
<td>0.3084 0.3527</td>
<td>38.3</td>
<td>0.9</td>
</tr>
<tr>
<td>MBNi</td>
<td>0.3086 0.3525</td>
<td>37.8</td>
<td>0.6</td>
</tr>
<tr>
<td>MBFe</td>
<td>0.3089 0.3523</td>
<td>38.5</td>
<td>1.9</td>
</tr>
<tr>
<td>MBSS</td>
<td>0.3086 0.3525</td>
<td>38.2</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Figure 5.2 illustrates the $dc$ magnetic susceptibility plots in ZFC condition for Cu, Ni, Fe and SS added MgB$_2$ samples. All the samples show superconducting transitions with $T_C$ in the range 37.8-38.5 K irrespective of the additives. But the near constant values of $T_C$ and the lattice parameters observed clearly point out that the additives do not substitute at either Mg or B sites. 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 the same and that of MBNi sample is slightly lower (37.8 K). The samples MBSS and MBFe exhibit positive magnetization above transition temperature due to the paramagnetic or ferromagnetic nature of the additives.
Figure 5.2: DC magnetic susceptibility vs temperature plots of MgB$_2$ samples added with Cu, Ni, Fe and SS

As shown in figure 5.3, $J_c(H)$ characteristics imply that the intragrain $J_c$ of Fe added MgB$_2$ sample attains better values among all samples. At higher fields, MBSS and MBFe samples show larger $J_c$ than the other samples containing reacted phases, which implies that there is a direct
correlation of $J_C$ with their superconducting core fraction and phase purity. The steep drop in $J_C$ at higher fields in all samples is attributed to the flux penetration into the grain boundaries, which 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.

5.2.3: Conclusion

The study shows the significant role of the reactivity of sheath material with Mg/B on the phase formation and superconducting properties of MgB$_2$. Absence of appreciable change in lattice parameters and $T_C$ point out that the additives are not substituted at either Mg or B sites in MgB$_2$. The additives Cu and Ni react with Mg/B and the reacted phases reduce the volume fraction of superconducting core and impede intergrain connectivity resulting lower $J_C$ at higher fields. On the other hand, Fe and SS added samples give higher volume fraction of MgB$_2$ core and hence better $J_C(H)$ characteristics which infers that Fe and SS are more suitable as sheath materials in MgB$_2$ wire fabrication.

5.3: Effect of processing temperature on the transport critical current of MgB$_2$/Fe superconducting wires

5.3.1: Introduction

Because of the huge difference in the melting points of Mg (650 °C) and B (2080 °C), there is hardly any scope for liquid-liquid reaction between the two; but reactions are feasible for solid-solid, solid-liquid and solid-gas interactions depending on the processing temperature. This in turn has a vital influence on the phase formation, microstructure, density and critical current of the MgB$_2$ superconductor. Based on various synthesis methods and nature of starting materials, many groups reported [17-18] that a heat treatment of 650-800 °C is required for the preparation of in situ MgB$_2$ wires. In the previous section, the influence of reactivity of different sheath materials such as Cu, Ni, Fe and SS on phase evolution and superconducting properties of MgB$_2$ has been discussed. Of these, Fe and its alloy SS seem to be the best among the sheath materials studied in achieving high $J_C$ due to their chemical compatibility with Mg and B and
hence Fe is chosen as suitable sheath material for preparing MgB$_2$ wires due to its better mechanical workability than SS. Usually, heat treatment is done in vacuum or inert atmosphere in order to avoid Mg oxidation. Fabrication of MgB$_2$ wires would become much easier if the vacuum/inert atmosphere condition could be avoided. Hence, a simple ‘capping technique’ has been introduced for the end sealing of MgB$_2$ wires so as to heat treat them directly in air. As the processing conditions of bulk synthesis are entirely different from that of wire making, further optimization of the processing temperature is essential for preparing good quality MgB$_2$ wires with high performance. Therefore, the present chapter investigates the effect of processing temperature on the phase evolution, microstructure and transport critical current of MgB$_2$/Fe wires. A temperature range of 600-800 °C is chosen for this study.

5.3.2: **Preparation and characterization of MgB$_2$/Fe monofilamentary wires**

Fe tubes (OD/ID = 5/3 mm) of length 5 cm were used for the fabrication of short length monofilamentary wires. The tubes were then filled with stoichiometrically weighed and homogenously mixed Mg+B powder and mechanically compacted. Copper studs were used as plugs to seal the ends of the tubes and both ends were crimped mechanically. The composite tube was then groove rolled down to the desired dimensions typically 1.33 mm and about 1 m in length, without any intermediate annealing. A schematic diagram for the preparation of monofilamentary MgB$_2$/Fe wires is shown in figure 5.4 and a photograph of wire rolling process is shown in figure 5.5. The rolled monofilamentary wire was then cut into pieces of 10 cm length and these pieces were end sealed before heat treatment in air. The end sealing was done by a ‘capping technique’ where the ends of the conductors were inserted into suitable iron tubes of short length (1.5 cm) and mechanically fixed with the conductor using a hydraulic press. Then, the ends of the Fe tubes were welded using dc arc without any flux, by keeping the sample cooled using a wet cloth.
Figure 5.4: A schematic diagram of the preparation procedure of monofilamentary MgB₂ wires

Figure 5.5: Photograph of groove roller and wire rolling

Samples were then heat treated directly in air at desired temperatures in a programmable muffle furnace with a ramp rate of 5 °C/minute and subsequently furnace cooled. The Fe sheathed MgB₂ wire is then used for transport measurements after thoroughly removing the slight layer of FeO. For XRD and SEM analysis, MgB₂ core was taken out by mechanically peeling off the Fe sheath. The samples heat treated at temperatures 600, 625, 650, 675, 700, 750 and 800 °C for 2 hrs are labeled
as MB600, MB625, MB650, MB675, MB700, MB750 and MB800 respectively.

The structural and phase analysis of the samples were performed using an X-ray diffractometer. Phase identification of the samples was performed using X’Pert Highscore Software in support with ICDD PDF II database. The grain morphology and microstructure were examined by SEM. The $R-T$ and $I-V$ measurements were carried out by employing a heavy duty cryocooler interfaced cryostat using $dc$ four probe resistive method with the criterion of 1 $\mu$V/cm. The transport $J_C$ was obtained by dividing $I_C$ by the cross sectional area of MgB$_2$ core.

5.3.3: Results and discussion

![XRD pattern of MgB$_2$ samples processed at different temperatures]

Figure 5.6 shows the XRD patterns of MgB$_2$ monofilamentary wire samples processed at 600-800 °C. Since the formation of MgB$_2$ starts at 600 °C, the sample heat treated at 600 °C shows lesser amount of MgB$_2$ and higher amount of unreacted Mg. However, MgB$_2$ peaks become sharper and stronger and peaks of unreacted Mg decrease as the processing temperature increases which indicate increase in phase purity and crystallinity. On the boron rich side, no peaks of MgB$_4$ and MgB$_{12}$ phases were detected, which could be ascribed to the successful prevention of Mg evaporation at these heat treatment conditions. Moreover, absence of the peaks corresponding to
Fe and Fe containing compounds up to 750 °C indicates that there is no interfacial reaction occurring between the Fe sheath and Mg/B/MgB2 at these temperatures. The presence of minor amount of FeB2 phase in MB800 points out that its formation starts around this temperature. The traces of MgO detected in XRD may be due to the entrapped air in the reaction mixture. From XRD patterns, semi quantitative phase analysis of the samples processed at different temperatures are calculated and tabulated in table 5.3. As the processing temperature increases, the volume percentage of MgB2 increases with a corresponding decrease in Mg. But the sample sintered at 800 °C shows the presence of impurity phases such as FeB2 and consequently volume percentage of MgB2 reduces. MgO content is more or less same in all the samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Vol. % of</th>
<th>Lattice parameters (nm)</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MgB2</td>
<td>Mg</td>
<td>Others</td>
</tr>
<tr>
<td>MB600</td>
<td>7.8</td>
<td>92.2</td>
<td>0</td>
</tr>
<tr>
<td>MB625</td>
<td>62.1</td>
<td>36.1</td>
<td>1.8</td>
</tr>
<tr>
<td>MB650</td>
<td>80.8</td>
<td>16.5</td>
<td>2.7</td>
</tr>
<tr>
<td>MB675</td>
<td>84.9</td>
<td>12.3</td>
<td>2.8</td>
</tr>
<tr>
<td>MB700</td>
<td>89.1</td>
<td>7.9</td>
<td>3.0</td>
</tr>
<tr>
<td>MB750</td>
<td>92.7</td>
<td>4.5</td>
<td>2.8</td>
</tr>
<tr>
<td>MB800</td>
<td>85.8</td>
<td>1.1</td>
<td>13.1</td>
</tr>
</tbody>
</table>

The lattice parameters were calculated from XRD for hexagonal structure and tabulated (table 5.3). The samples show no significant variations in lattice parameters, within the experimental error. FWHM of (100), (101), (002) and (110) peaks of the samples processed at different temperatures is shown in figure 5.7. FWHM of all the peaks decreases significantly on increasing the sintering temperature indicating the increase in grain size of MgB2 with temperature. To analyze the effect of grain size on peak broadening, microstructural examination is also carried out using SEM. Figure 5.8 shows typical SEM images of the fractured MgB2 core of the wire samples heat treated at 625, 650, 700 and 800 °C. The samples show fine hexagonal and randomly oriented MgB2 grains with excellent
connectivity. The SEM images also show that the average grain size of the crystalline MgB$_2$ increases with sintering temperature, well in agreement with the decrease of FWHM from XRD.

Figure 5.7: Variation of FWHM of the core of the MgB$_2$/Fe wires with processing temperature

Figure 5.8: Typical SEM images of the core of the MgB$_2$/Fe wires processed at 625, 650, 700 and 800 °C
Figure 5.9: $R$-$T$ plots of MgB$_2$/Fe wire samples processed at different temperatures. Inset shows the enlarged portion of $R$-$T$ plot near the superconducting transition region.

Figure 5.10: Variation of transport $I_C$ and $J_C$ of MgB$_2$/Fe wire samples with processing temperature.
Figure 5.9 shows the temperature dependence of the normalized resistance of the MgB$_2$/Fe wires processed at different temperatures. All samples show sharp superconducting transitions and the observed $T_C$ is tabulated in table 5.3. It is found that $T_C$ increases systematically with processing temperature. This suggests that better crystallinity is achieved with higher processing temperatures. Relatively poor crystallinity in samples prepared at lower temperatures points to disorder in the crystal lattice, which leads to lower $T_C$.

The measurement of self-field transport current properties of MgB$_2$/Fe wires for different processing temperatures has been done at 7 and 30 K (figure 5.10). As seen from the graph, transport currents at both 7 and 30 K are found to be increasing systematically with the processing temperature, up to 650 °C. Among all samples, the one processed at 650 °C gives the highest transport current of $1.19 \times 10^5$ and $2.61 \times 10^4$ A/cm$^2$ at 7 and 30 K respectively. It is to be noted that the sample sintered at 650 °C contains only 80.8 % MgB$_2$ and it contains 16.5 % Mg. There were reports of better superconducting properties in MgB$_2$/Fe samples with excess Mg addition [19, 20]. Hence, the presence of unreacted Mg in moderate amount in the MgB$_2$ matrix helps in better connectivity. Moreover, both FWHM and SEM analysis confirm that grain size increases with the processing temperature. In the case of MgB$_2$, the grain boundaries can act as flux pinning centers and hence the grain size has significant role in enhancing the critical current at both self-field and in-field. The slight decrease in $J_C$ of samples processed at higher temperatures is due to the decrease in the amount of unreacted Mg and increase in grain size, while the formation of non-superconducting phases such as FeB$_2$ causes significant reduction of $J_C$ in the sample processed at 800 °C.

5.3.4: Conclusion

The effect of processing temperature on phase formation, microstructure and transport critical current of MgB$_2$/Fe monofilamentary wire samples processed at temperatures 600-800 °C were studied. All samples show a systematic increase in MgB$_2$ phase formation and $T_C$ except for the sample processed at 800 °C. At lower processing temperatures, the crystallinity and grain size of MgB$_2$ formed will be lesser and hence
contains more structural defects and grain boundaries. The sample processed at 650 °C gave the best self-field transport $J_C$ value of $1.19 \times 10^5$ A/cm$^2$ at 7 K. The presence of reasonable amount of unreacted Mg and the reduced grain size are the reasons for enhancing the critical current of the sample processed at 650 °C.

5.4: Influence of nano Cu additive on MgB$_2$ phase formation, processing temperature and transport properties

5.4.1: Introduction

Doping of various elements and compounds has been attempted in order to fabricate in situ MgB$_2$ bulk and wires with high critical current density. However, most of these doped samples were fabricated at high temperatures above 650 °C and very often the sheath materials reacted with Mg/B at elevated temperatures. Moreover, processing at higher temperatures causes higher volatile loss of Mg and significant increase in the formation of MgO, which weakens the grain to grain connectivity in MgB$_2$ matrix [21, 22]. In order to avoid these problems, some recent studies have concentrated on the low temperature solid state sintering method to prepare pure or doped MgB$_2$ samples with improved $J_C$. Yamamoto et al. obtained pure MgB$_2$ samples by processing at 600 °C for 60 hrs [23]. Rogado et al. prepared pure MgB$_2$ bulk by processing at 550 °C for 16 hrs with an intermediate grinding step with improved $J_C$ [24]. However, the reaction between Mg and B at 550 °C needed a very long time to form the complete MgB$_2$ phase due to the low diffusion rate of atoms in the solid state below the melting point of Mg. Some reports suggested that use of MgH$_2$ or nano sized Mg particles and high quality B powder as starting materials were effective in lowering the synthesis temperature of MgB$_2$ samples, but heating above 600 °C was essential to form the MgB$_2$ phase [25-28].

Recently, some efforts on lowering of synthesis temperature of MgB$_2$ were made by the addition of suitable metal powders into the system [29-33]. It was observed that the metal doping introduced liquid phase during the reaction which assisted the phase formation of MgB$_2$. Among these methods, Cu doping proved to be the most effective. However, the
results reported so far on Cu doped MgB$_2$ have been limited to magnetic measurements. The major concern is whether the material can carry large transport $J_C$. In this work, effect of nano Cu additive on phase formation, processing temperature and transport properties of MgB$_2$ is focused. Mg, amorphous B, Cu nano powder (<100 nm, 99.8 %) and commercially available Fe tubes were used for processing. The tubes were filled with homogeneously mixed pure (Mg+B) and doped (Mg+B+2.5 wt% Cu) powders and mechanically compacted. The reason for choosing 2.5 wt% Cu is explained in the subsequent section. The composite tubes were then groove rolled into wires of 1.33 mm OD. These were cut into short length (10 cm) samples and end sealed. The sealed wires were then heat treated directly in air at 550, 575, 600, 625, 650 and 675 °C for 2 hrs in a muffle furnace and subsequently cooled by switching off the furnace.

5.4.2: Results and discussion

![Figure 5.11: XRD patterns of pure MgB$_2$ samples processed at different temperatures (550-675 °C)](image)

*Figure 5.11* shows the XRD patterns of pure MgB$_2$ samples processed at temperatures varying from 550 °C to 675 °C. The first three samples processed at 550, 575 and 600 °C which are well below the melting point of Mg exhibit almost similar patterns. It is found that starting Mg
remained as the main phase with small peaks of MgB$_2$. The rate of diffusion is not high enough to form considerable amount of MgB$_2$ within two hours at these temperatures. But when the processing temperature increases to 625 °C, diffusion rate increases and hence the formation rate of MgB$_2$ also increases. At higher temperatures, Mg starts melting and the reaction rate is further enhanced. But some unreacted Mg can be seen in these samples, because temperature/duration is insufficient for complete formation of MgB$_2$. However, it is reported that an optimum amount of excess Mg is helpful in improving $J_c(H)$ behavior of MgB$_2$ [34].

Figure 5.12: XRD patterns of nano Cu added MgB$_2$ samples processed at different temperatures (550-675 °C)

Figure 5.12 shows the XRD patterns of Cu added samples processed at temperatures similar to pure samples. It can be seen that, at 550 °C itself remarkable quantity of MgB$_2$ has been formed. As the temperature increases, the Mg content reduces and MgB$_2$ content improves. Some trace of MgO is observed in both pure and Cu added samples at higher temperatures. Since the size of Cu particles used in the present work are much smaller and are more reactive than the B particles, in MBCu samples Mg reacts first with Cu forming the Mg$_2$Cu phase. As a result, the presence of local Mg$_2$Cu liquid phase (melting point of Mg$_2$Cu is ~550 °C) could
accelerate the reaction between Mg and B and finally results in the formation of MgB$_2$ phase even at such low temperatures. The peak intensity of Mg$_2$Cu remains constant throughout the entire range of temperatures, which indicates that the formation of Mg$_2$Cu is saturated at 550 °C itself. In figure 5.12, it can also be observed that the peak positions of the MgB$_2$ phase in the Cu added samples remain unchanged, which indicates that there is no Cu substitution in MgB$_2$.

![Image](image1.png)

**Figure 5.13: Variations of FWHM of (100), (101), (002) and (110) peaks of pure and Cu added MgB$_2$ samples**

From the XRD, the FWHM values of (100), (101), (002), and (110) peaks of pure and Cu added MgB$_2$ are shown in figure 5.13. It can be seen that the FWHM values steadily decrease with the increase in processing temperature for both pure and Cu added MgB$_2$ samples indicating the increase in grain size of MgB$_2$ with temperature. The pure sample exhibits higher FWHM values compared to Cu added samples at identical processing temperatures. Further, the results are correlated with the microstructure of the samples. *Figure 5.14 shows the SEM images of both pure (625 and 650 °C) and Cu added (550, 575, 600 and 650 °C) MgB$_2$ samples. For pure samples, MgB$_2$ grains of relatively smaller size have been formed compared to corresponding Cu added samples at the same*
temperature. The SEM images of Cu added samples show small MgB$_2$ grains starting from 550 °C itself. It is clear that addition of Cu not only accelerates the formation of the MgB$_2$ phase but also improves the crystallinity and grain connectivity of MgB$_2$ appreciably as the processing temperature increases. Another point to be noted from the microstructures is that the density of Cu added samples is distinctly higher than that of pure MgB$_2$ samples.

Figure 5.14: SEM images of the fractured surfaces of pure MgB$_2$ sample heat treated at (a) 625 °C and (b) 650 °C and Cu added MgB$_2$ samples heat treated at (c) 550 °C, (d) 575 °C, (e) 600 °C and (f) 650 °C

Figure 5.15 compares the temperature dependence of resistance for pure MgB$_2$ sample processed at 650 °C and Cu added sample at 550 °C. As shown, these samples exhibit sharp superconducting transitions with $T_C$
around 38 K and a transition width, $\Delta T_C < 1.5$ K. It is observed that for nano Cu added sample the superconducting transition remains sharp at 38 K which implies that Cu is not substituted at Mg/B sites and the impurities formed have little effect on $T_C$.

![Figure 5.15: Temperature dependence of resistance for pure MgB$_2$ sample processed at 650 °C and Cu added sample at 550 °C](image)

The measurement of self-field transport current properties of Cu doped MgB$_2$ wires has been done and compared with those of the pure MgB$_2$ wires for different processing temperatures (figure 5.16). As seen from the graph, $J_C$ of Cu added MgB$_2$ wire measured at 30 K is higher compared to the corresponding pure MgB$_2$ wires till the processing temperature reaches 650 °C. The transport $J_C$ of Cu added wire processed at 550 °C ($2.2 \times 10^4$ A/cm$^2$) is quite comparable with that of Cu-free wire processed at 650 °C ($2.5 \times 10^4$ A/cm$^2$). At/above 650 °C, both the samples exhibit nearly same critical current densities and the $J_C$ is found to be slightly lesser for both samples beyond 650 °C. This may be due to the slight increase in MgO formation at the grain boundaries, in these samples. The highly enhanced critical current density for Cu added samples prepared at lower temperatures is due to the enhanced rate of formation of MgB$_2$ at lower temperatures. The selection of weight percentage of Cu as 2.5 was
done on the basis of $J_C$ measurements of MgB$_2$ wires with varying weight percentage of Cu processed at 600 °C (inset of figure 5.16). Among which 2.5 wt% of Cu yielded the highest $J_C$.

![Figure 5.16: Variation of \(J_C\) with processing temperatures of pure and Cu added MgB$_2$ samples at 30 K. Inset shows variation of \(J_C\) with wt% of Cu added in the MgB$_2$ samples processed at 550 °C.](image)

**5.4.3: Conclusion**

The effects of nano Cu addition on the superconducting properties of MgB$_2$/Fe wires were studied. Both pure and Cu added samples were prepared by *in situ* PIT method and processed at different temperatures ranging from 550-675 °C. It was found that the MgB$_2$ can be synthesized at around 550 °C with minor Cu addition, which offers a substantial reduction in the processing temperature compared to that of pure MgB$_2$. All the Cu added samples processed below 650 °C showed enhanced transport $J_C$ values compared to the Cu-free samples. The transport $J_C$ of Cu added wire processed at 550 °C is quite comparable with that of Cu-free wire processed at 650 °C. The added nano Cu preferentially reacts with Mg and forms Mg$_2$Cu which melts at around 550 °C. The liquid phase thus formed assists the formation of MgB$_2$ at a lower temperature.
5.5: Preparation of MgB$_2$/Fe superconducting tapes with highly densified core by hot-pressing of \textit{in situ} PIT wires

5.5.1: Introduction

A major problem in the manufacture of MgB$_2$ conductors is their high porosity. This is severe in the case of \textit{in situ} preparation in which only around 50\% of theoretical density could be achieved in many cases. This is mainly caused by the low packing density of Mg and B powder mixture and the volume shrinkage during the \textit{in situ} formation of MgB$_2$. The porosity limits the active current carrying area fraction and also weakens the grain connectivity. Measures to reduce porosity of MgB$_2$ have been taken since its discovery by adopting hot isostatic pressing or high pressure sintering with excellent results [35-37]. However, most of the works are limited to \textit{ex situ} process and also the methods have limitations in making long length conductors. \textit{In situ} process is more flexible with respect to chemical doping and hence leads to MgB$_2$ with improved performance in higher magnetic fields. Flükiger’s group reported making of \textit{ex situ} MgB$_2$ tapes by a conventional hot rolling method, wherein the roller has been heated to high temperatures [38]. By this method, they have studied the effect of rolling on the anisotropy and texture gradient of MgB$_2$ tapes with respect to the particle size of the precursor. However, energy required for heating up the massive roller for large scale production of thin MgB$_2$ tapes is considerably high.

In this work, we report a simple, energy efficient and inexpensive method for preparation of Fe-sheathed MgB$_2$ conductors with high core density and critical current by hot-pressing of \textit{in situ} PIT wires. Compared to the conventional hot rolling method this method is energy efficient as the sample itself is heated instead of the massive roller. The method also significantly reduces the oxidation and evaporation loss of Mg and has many advantages such as less preparation cost and power consumption due to the avoidance of special furnaces with inert gas atmosphere. With suitable engineering, the present method can be transformed into a hot rolling process for the continuous production of high quality MgB$_2$ conductors.
5.5.2: Preparation and characterization of hot-pressed MgB$_2$ tapes

Mg, amorphous B and Fe tubes of suitable dimensions were used for the preparation of PIT wires. The tubes were filled with homogeneously mixed Mg and B powders and mechanically compacted. The composite tubes were then groove rolled into wires of 1.47 mm OD. Samples of length 20 cm were used for hot-pressing after end sealing. In this work, PIT wire was heated by passing a suitable current, followed by pressing in hot conditions with the help of a hydraulic press.

![Figure 5.17: (a) Schematic diagram and (b) photograph of the experimental set up for hot-pressing](image)

The system for electrical self-heating and hot-pressing mainly consists of a programmable current source (DC), hydraulic press and the sample anchored horizontally as shown in figure 5.17 (a) and (b). The sample is positioned such that it is aligned parallel between the top and bottom plungers of the press. A thermocouple (TC) is kept very close to the uniform hot region outside the plunger area to monitor the temperature. The sample is heated by passing a suitable current through the sample, either manually or automatically through a PC interface. Temperature of the sample is increased at a ramp rate of 20 °C/min, soaked for a total period of 60 or 120 minutes at 700 °C, and then cooled at a rate of 20 °C/min to room temperature. During the soaking period, samples were pressed at a pressure of 500 MPa without putting off the power. Four sets of different samples were prepared with varying soaking durations, before and after pressing. The voltage and current readings during soaking were 3.2 V and 28 A respectively and the energy consumption for preparation of a typical sample...
with 60 min soaking was 0.11 kWh. Apart from these, a set of wire samples was prepared by electrical self-heating at 700 °C without pressing for comparison of microstructure and density with the hot-pressed ones. The sample details are given in table 5.4. Short length samples for characterizations were then selected by properly cutting out the hot-pressed area.

Phase analysis and microstructural investigation of the samples were performed using XRD and SEM. The density of the MgB$_2$ core was determined by hydrostatic method. Superconducting properties such as $R-T$ and $I_C$ measurements were carried out by employing a cryocooler interfaced cryostat by four probe resistive method.

5.5.3: **Results and discussion**

![XRD patterns](image)

**Figure 5.18: XRD patterns of self-heated and hot-pressed MgB$_2$ samples**

XRD patterns of the hot-pressed samples soaked for different durations before and after pressing are shown in figure 5.18. All the patterns contain MgB$_2$ as the major phase. Traces of MgO and some unreacted Mg are observed in all the samples. Minor amount of FeO is found in some samples which may be from the sheath material. Absence of FeB$_2$ peaks indicates that there is almost no (or very small) reaction between Fe sheath and B. **Figure 5.19** shows SEM images of fractured surface (both transverse sectional view and enlarged core view) of MgB$_2$ wire (SH60) prepared by self-heating alone and a tape (HP60) prepared by hot-pressing. The images
show distinct microstructural differences for the samples with and without hot-pressing. The core is observed to be significantly densified in the tape compared to the wire. The wire contains large pores, characteristic of the \textit{in situ} prepared MgB$_2$, caused by the low green density of the (Mg+B) mixture and the volume shrinkage during MgB$_2$ formation. On the other hand, the tape has highly dense core with well connected grains.

\textbf{Table 5.4: Soaking details, density and transport current of self-heated and hot-pressed MgB$_2$ samples}

<table>
<thead>
<tr>
<th>Samples</th>
<th>Soaking duration (min)</th>
<th>Density (g/cm$^3$)</th>
<th>$I_C$ (A)</th>
<th>$J_C$ ($\times 10^4$ A/cm$^2$) at 30 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before pressing</td>
<td>After pressing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SH60 60</td>
<td>60 (without pressing)</td>
<td>1.41</td>
<td>31</td>
<td>0.8</td>
</tr>
<tr>
<td>HP30 30</td>
<td>30</td>
<td>30</td>
<td>2.38</td>
<td>36</td>
</tr>
<tr>
<td>HP45 45</td>
<td>45</td>
<td>15</td>
<td>2.33</td>
<td>40</td>
</tr>
<tr>
<td>HP60 60</td>
<td>60</td>
<td>00</td>
<td>2.45</td>
<td>75</td>
</tr>
<tr>
<td>HP120 120</td>
<td>120</td>
<td>00</td>
<td>2.23</td>
<td>65</td>
</tr>
</tbody>
</table>

\textbf{Figure 5.19: SEM images of fractured surface of typical MgB$_2$ samples}
The core density of the self-heated and hot-pressed MgB$_2$ samples is also given in table 5.4. All the hot-pressed samples have significantly higher density compared to the sample prepared without pressing. The core density of the self-heated wire and the hot-pressed tape after a soaking duration of 60 min is found to be 1.41 and 2.45 g/cm$^3$ respectively which corresponds to 53.6% and 93.2% of the theoretical density of MgB$_2$ (2.63 g/cm$^3$). The increase in density was verified by estimating the volume reduction of the core by comparing the core area of the wire and tape with the help of an image analyzer. The volume reduction was estimated to be 41.8%, which matches with the increase in density.

![R-T plots of self-heated and hot-pressed MgB$_2$ samples](image.png)

Figure 5.20: R-T plots of self-heated and hot-pressed MgB$_2$ samples

Temperature dependence of the normalized resistance of all samples exhibit sharp superconducting transitions with $T_c$ around 38.5 K and a transition width, $\Delta T_c < 1$ K as observed in figure 5.20. The measurement of self-field transport current properties of self-heated and hot-pressed MgB$_2$ samples has been done at 30 K and tabulated in table 5.4.
The variation of $J_c$ of each sample is plotted in figure 5.21. Among the hot-pressed samples, critical current is minimum for HP30 and maximum for HP60. The $J_c$ values of all the hot-pressed samples are significantly higher compared to the self-heated wire sample (SH60). It is to be noted that the samples HP30, HP45 and HP60 have undergone a total period of 60 min soaking at 700 °C. For hot-pressed samples, $J_c$ is found to be increasing with the initial soaking duration (before pressing), up to 60 min. On the other hand, further increase in soaking duration shows a reduction trend in both density and $J_c$. The maximum $J_c$ achieved for the hot-pressed sample ($3 \times 10^4$ A/cm² at 30 K) is almost 4 times of that obtained for the self-heated sample soaked for the same duration without pressing. This clearly shows that for obtaining maximum $J_c$ the sample needs to be soaked for an optimum period before pressing, which is necessary for the maximum densification of MgB₂ core so as to achieve well connected grains for a maximum super current flow. The method described here can be engineered into a continuous hot rolling process with an array of groove rollers in tandem initially for wire making, followed by an arrangement for electrical self-heating and flat rolling at the end. This can produce highly densified high performance MgB₂ conductors.
5.5.4: Conclusion

A simple and easy method for preparation of *in situ* MgB$_2$ superconducting tapes with highly densified core has been demonstrated. The method comprises heating of the PIT wire by passing a suitable current, followed by pressing in hot conditions with the help of a hydraulic press. A core density of 2.45 g/cm$^3$ (93.2 % of theoretical density) and almost 4-fold increase in critical current are achieved for the best hot-pressed sample. The method is highly energy efficient since it uses electrical power only for heating the wire/tape whereas in conventional heat treatment process electrical power is required for heating a furnace loaded with the wire/tape.

5.6: Summary

The role of the reactivity of sheath material with Mg/B on the phase formation and superconducting properties of MgB$_2$ was studied. It was found that Cu and Ni react with Mg/B and the reacted phases reduce the volume of superconducting core and impede intergrain connectivity resulting lower $J_C$ at higher fields. On the other hand, in the case of Fe and SS, the samples give higher volume fraction of MgB$_2$ core and hence better $J_C(H)$ characteristics which infers that Fe and SS are more suitable as sheath materials in MgB$_2$ wire fabrication. The effect of processing temperature on phase formation, microstructure and transport critical current of MgB$_2$ monofilamentary wire samples processed at temperatures in the range 600-800 °C were also studied. The sample processed at 650 °C gave the best self-field transport $J_C$. The presence of reasonable amount of unreacted Mg and the reduced grain size are found to be the reasons for enhancing the critical current of the sample processed at 650 °C. The effects of nano Cu addition on the superconducting properties of MgB$_2$/Fe wires were studied. It was found that the MgB$_2$ can be synthesized at around 550 °C with minor Cu addition, which offers a substantial reduction in the processing temperature (by around 100 °C) compared to that of pure MgB$_2$. The added nano Cu preferentially reacts with Mg and forms Mg$_2$Cu which melts at around 550 °C. The liquid phase thus formed assists the formation of MgB$_2$ at a lower temperature. Fe sheathed *in situ* MgB$_2$ superconducting tapes with high densities were prepared by hot-pressing of electrically self-heated
PIT wires. The method comprises heating of the PIT wire by passing a suitable current, followed by pressing in hot conditions with the help of a hydraulic press. A core density of 2.45 g/cm³ (93.2 % of theoretical density) and almost 4-fold increase in critical current are achieved for the best hot-pressed sample.

References:


