Chapter 5

Improvement of self-field critical current density of MgB$_2$ for current lead applications

Since the discovery of MgB$_2$, majority of the work in this material was concentrated on improvement of in-field current density [1-7]. For applications in magnetic field this aspect is very important as the devices have to withstand high magnetic field. Normally current leads are operated at environment with little or a little magnetic field. In this circumstances field dependence of critical current is not significant factor for current lead applications. In this point of view, significant factors which are important for current lead applications are low cost, high current carrying capacity with low thermal conductivity and good mechanical properties. This chapter discusses excess addition of Mg while making MgB$_2$ wires. The results were very promising in point of view of current lead development. According to our perception, addition of excess Mg is expected to degrade the superconducting properties instead it was found to improve the self-field properties. This is very attractive in application point of view as it reduces production cost, improves mechanical properties and improves self-field superconducting properties without adding much to thermal conductivity of wires. Production cost will be reduced significantly since the cost of Mg is much less than that of B. Mg is easily available also. As current leads are huge devices in present day applications such as LHC, superconducting material cost is as important as operational cost.
In this chapter, the structural and superconducting properties of excess Mg added MgB\textsubscript{2} superconducting wires were investigated and compared with normal stoichiometric MgB\textsubscript{2} samples. The samples were prepared by \textit{in situ} powder in tube (PIT) solid state method.

### 5.1 Introduction

Owing to mechanically hard and brittle nature of MgB\textsubscript{2}, the powder in tube (PIT) technique has been widely used for conductor fabrication in the form of wires and tapes [8-14]. For MgB\textsubscript{2} conductors, transport critical current density is the real useful $J_c$ that flows through the whole of the sample and it depends on the connectivity between individual MgB\textsubscript{2} grains [15]. The porous microstructure, micro-cracks and the presence of amorphous regions or the insulating oxide layers in the grain boundaries obstruct the current path and decrease the effective grain connectivity [16]. Due to volume reduction during the chemical reaction between Mg and B, the typical packing density in MgB\textsubscript{2} bulks, wires and tapes is found to be as low as 50 % of the theoretical density (2.62 g/cm\textsuperscript{3}). Moreover, most of MgB\textsubscript{2} superconductors were synthesized by sintering at temperatures above melting point of Mg, which generally caused porosities and lower density as a result of the higher volatile loss of Mg [17-19]. Processing at higher temperatures is equally responsible for the reactivity of sheath materials with Mg/B and the significant increase in MgO formation, which weakens the grain connectivity in MgB\textsubscript{2} matrix [20-21]. In order to avoid these disadvantages, some studies have concentrated on the low temperature solid state sintering method to prepare pure or doped MgB\textsubscript{2} samples with improved $J_c$ [22-25]. A limitation of this technique, however, is the increased time for the reaction between Mg and B at low temperatures to form the complete MgB\textsubscript{2} phase. This is due to the decreased atomic diffusion rate in the solid state below the melting point of Mg. Inversely, if formation of MgB\textsubscript{2} phase is incomplete, then the residual
Mg and B present in these samples can significantly influence the structural and superconducting properties of MgB$_2$. Hence, many techniques such as ball milling of the starting materials, use of different Mg-based precursors and assisted sintering with different metal or alloy additions have been employed to enable processing at lower temperature and to reduce the processing time of MgB$_2$ while improving its superconducting properties [26-31]. There have been reports on considering slightly excess magnesium so as to compensate for the anticipated Mg loss, but to the best of our knowledge, there are only a few systematic studies [32, 33] of taking excess Mg, and only some of these follow in situ method. However, the reports suggest that even slight excess Mg addition could prevent Mg loss and improve the normal state properties, grain connectivity and critical current.

In one of our experiments, we attempted to prepare MgB$_2$ superconducting wires using stoichiometric Mg and B powders by processing at a relatively low temperature of 600 °C (5 h). Surprisingly, we observed a consistent and distinct enhancement of transport critical current in these wires when compared to the normal wire samples prepared at 700 °C/2 h, even though the formation of MgB$_2$ phase in former wires is far from completion and a large amount of residual Mg is still present. This has motivated us to increase the Mg stoichiometry from one to many folds in steps and prepared wires (hereafter called as Mg/MgB$_2$ composites wires) by heat treating at 600 °C (5 h). In order to elude the excess amount of unreacted amorphous B corresponding to that of unreacted Mg and to fill the related amount of Mg inside the voids and grain boundaries, excess Mg is heavily added. Accordingly, normal state properties, grain connectivity and transport current are found to be enhanced without much affecting $T_C$ against the expectation. This result seems to bring a new opportunity for the development of low cost practical MgB$_2$ superconductors with improved self-field transport $J_C$. 
5.2 Experimental details

Mg powder (<105 µm, 99.8 % purity), amorphous B powder (<44 µm, 99 % purity), and commercially available Fe tubes were used for the in situ PIT wires. Fe tubes of length 6 cm, outer diameter (OD) 6 mm and inner diameter (ID) 4 mm were used for the fabrication of wires. The tubes were filled with homogeneously mixed precursor powders (xMg+2B, where x=1 to 7) and mechanically compacted. Details of preparation of the wires are described under section 4.1.2. The wires were heat treated at 600 °C (5 h) in a muffle furnace with a ramp rate of 10 °C/min and subsequently cooled by switching off the furnace (samples 1MG to 7MG). Normal stoichiometric MgB₂ sample was also prepared by heat treating at 700 °C (2 h) (RMG) as reference sample.

The structural and phase analysis of the samples were done using an X-Ray Diffractometer (Philips X’pert Pro) with Cu Kα radiation employing a proprietary detector, X’Celerator and a monochromator at the diffracted beam side in the Bragg-Brentano configuration. Samples for the XRD analysis were recovered from the wires by mechanically peeling off the Fe sheath and powdering the reacted core and the patterns were taken using a zero background holder. Phase identification of the samples were performed using X’Pert Highscore Software in support with ICDD-PDF-2 database. Microstructural investigation of the samples was done using an optical microscope (Leitz-Metalloplan). Transport critical current ($I_C$) measurements at various temperatures were carried out by employing a heavy duty cryocooler interfaced cryostat (Cold head Model: SHI SRDK-408) using DC four probe resistive method. The measurements were conducted by passing currents in steps for short durations (100 ms to 1 s) and providing cooling time (5 -10 s) after each step using LabVIEW software.
5.3 Results and discussion

The XRD patterns of the Mg/MgB$_2$ composites prepared at 600 °C (5 h) by varying the Mg stoichiometry from 1 to 7 (samples designated as 1MG to 7MG respectively) are shown in figure 5.1. The pattern of a stoichiometric MgB$_2$ sample, heat treated at 700 °C (2 h) is also presented in the same figure as a reference sample (RMG) wherein MgB$_2$ is found to be the main phase with some traces of MgO. Whereas for the Mg/MgB$_2$ composite, 1MG, it can be seen that the formation of MgB$_2$ phase is not complete and a large amount of unreacted Mg is present. This is because the rate of diffusion of Mg in the solid state is not adequate for the complete formation of MgB$_2$ at a temperature well below 650 °C, the melting point of Mg. The weight fraction of Mg and MgB$_2$ in each sample was determined from the XRD pattern shown in figure 5.2.
Figure 5.2 Weight fraction of Mg and MgB$_2$ in the composites as a function of initial Mg stoichiometry

Figure 5.2 shows that on increasing the stoichiometric amount of Mg, the relative amount of residual Mg in the composites increases while that of MgB$_2$ decreases. On comparing the composite samples with the reference sample, it is seen that formation of undesirable MgO is completely suppressed in the composites obviously due to the lower processing temperature. Table 5.1 Contains sample details, heat treatment conditions and volume percentage of phases.

Table 5.1 Sample details, heat treatment and vol.% of phases

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Sample details</th>
<th>Heat treatment temperature / duration</th>
<th>Vol.% of phases</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>MgB$_2$</td>
</tr>
<tr>
<td>RMG</td>
<td>1Mg+2B</td>
<td>700 °C/2h</td>
<td>100</td>
</tr>
<tr>
<td>1MG</td>
<td>1Mg+2B</td>
<td>600 °C/5h</td>
<td>65.5</td>
</tr>
<tr>
<td>2MG</td>
<td>2Mg+2B</td>
<td>600 °C/5h</td>
<td>44.6</td>
</tr>
<tr>
<td>3MG</td>
<td>3Mg+2B</td>
<td>600 °C/5h</td>
<td>33.1</td>
</tr>
<tr>
<td>4MG</td>
<td>4Mg+2B</td>
<td>600 °C/5h</td>
<td>24.8</td>
</tr>
<tr>
<td>5MG</td>
<td>5Mg+2B</td>
<td>600 °C/5h</td>
<td>16.5</td>
</tr>
<tr>
<td>6MG</td>
<td>6Mg+2B</td>
<td>600 °C/5h</td>
<td>13.2</td>
</tr>
<tr>
<td>7MG</td>
<td>7Mg+2B</td>
<td>600 °C/5h</td>
<td>10.9</td>
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The self-field transport current of the Mg/MgB$_2$ composite wires has been measured with respect to temperature (10-30 K) and compared with that of the reference sample figure 5.3.

Figure 5.3 Critical current density vs. temperature of stoichiometric and excess Mg added samples

The phase assemblage of the composites shows that the formation of MgB$_2$ phase is incomplete and there is a large amount of residual Mg present in these samples (figure 5.2). But it is seen that these large fractions of residual Mg assist to enhance the $J_c$ instead of degrading it. Moreover, on increasing the amount of Mg, the critical current density is found to increase significantly up to an optimum Mg stoichiometry of 6 (sample 6MG) beyond which it decreases. The self-field $J_c$ increases from $1.15 \times 10^5$ A/cm$^2$ (RMG)/$1.36 \times 10^5$ A/cm$^2$ (1MG) to $5.20 \times 10^5$ A/cm$^2$ (6MG) at 10 K. Remarkably, the sample 6MG which has shown the highest $J_c$ contains around 86.8% Mg and around 13.2% MgB$_2$ (assuming that no other phase has formed). It is to be noted that the composite samples from 1MG to 4MG show enhanced current carrying capability throughout the whole range of temperature studied (10-30 K) whereas the $J_c$ of 5MG, 6MG and 7MG samples has a decreasing trend at higher temperatures near to the
transition region. The decreasing trend may be due to their slightly lower $T_c$ and higher $\Delta T_c$ values which will be discussed in the succeeding sections.

To further investigate the effect of increased levels of Mg on superconducting properties, the temperature dependence of resistivity of Mg/MgB$_2$ composites wire samples is carried out after peeling off the Fe sheath. Figure 5.4 shows the $\rho(T)$ plots of the composite wires, a pure Mg wire sample and the inset shows an enlarged view of the $\rho(T)$ curve near superconducting transition. As observed, the normal state resistivity of the composite wires reduces drastically as the Mg content increases. The highest resistivity is shown by the reference sample, RMG while the sample 1MG shows the next lower resistivity. The lowest resistivity is recorded by the pure Mg wire from room temperature to the transition temperature of MgB$_2$.

![Figure 5.4 Resistivity vs. temperature of Mg metal (Mg), referred MgB$_2$ (RMG) and stoichiometric (1MG) and excess Mg added MgB$_2$ samples. Inset shows the enlarged view near superconducting transition.](image)
Table 5.2 Critical parameters of the samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_C$ (K)</th>
<th>$\Delta T_C$ (K)</th>
<th>$\rho_{300}$ (µΩcm)</th>
<th>$\rho_{40}$ (µΩcm)</th>
<th>$\Delta \rho$ (µΩcm)</th>
<th>RRR</th>
<th>$A_F$ (%)</th>
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<tr>
<td>RMG</td>
<td>38.78</td>
<td>1.1</td>
<td>32.8</td>
<td>5.17</td>
<td>27.65</td>
<td>6.35</td>
<td>15.55</td>
</tr>
<tr>
<td>1MG</td>
<td>38.72</td>
<td>1.83</td>
<td>31.1</td>
<td>3.54</td>
<td>27.56</td>
<td>8.79</td>
<td>15.60</td>
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<tr>
<td>2MG</td>
<td>37.64</td>
<td>1.02</td>
<td>21.05</td>
<td>1.36</td>
<td>19.69</td>
<td>15.48</td>
<td>21.84</td>
</tr>
<tr>
<td>3MG</td>
<td>37.71</td>
<td>0.75</td>
<td>9.45</td>
<td>0.388</td>
<td>9.062</td>
<td>24.36</td>
<td>47.45</td>
</tr>
<tr>
<td>4MG</td>
<td>37.55</td>
<td>0.7</td>
<td>9.46</td>
<td>0.37</td>
<td>9.09</td>
<td>25.57</td>
<td>47.30</td>
</tr>
<tr>
<td>5MG</td>
<td>37.48</td>
<td>0.89</td>
<td>8.87</td>
<td>0.319</td>
<td>8.551</td>
<td>27.81</td>
<td>50.29</td>
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<tr>
<td>6MG</td>
<td>37.28</td>
<td>1.21</td>
<td>7.6</td>
<td>0.284</td>
<td>7.316</td>
<td>26.76</td>
<td>58.78</td>
</tr>
<tr>
<td>7MG</td>
<td>37.07</td>
<td>1.25</td>
<td>7.5</td>
<td>0.295</td>
<td>7.205</td>
<td>25.42</td>
<td>59.68</td>
</tr>
</tbody>
</table>

Table 5.2 illustrates the values of $T_C$-onset ($T_C$), transition width ($\Delta T_C$), room temperature resistivity ($\rho_{300}$), resistivity near transition ($\rho_{40}$), change in phonon term resistivity ($\Delta \rho=\rho_{300}-\rho_{40}$), residual resistivity ratio (RRR=$\rho_{300}/\rho_{40}$) and the Rowell connectivity factor ($A_F$) of the Mg/MgB$_2$ composites and the reference MgB$_2$ sample. It is observed that the composite sample 1MG which contains stoichiometric Mg and B shows almost identical $T_C$ value (38.72 K) with respect to RMG (38.78 K) which decreases marginally with increase in the addition level of Mg and the minimum $T_C$ is obtained for 7MG (37.07 K). The $T_C$ of the sample 6MG which showed the maximum $J_C$ has decreased only by 1.50 K with respect to the reference MgB$_2$ sample. Analyzing the transition width $\Delta T_C$ (defined as the difference between $T_C$-onset and $T_{C0}$, the temperature at which $\rho$ tends to zero), the sample 1MG exhibits more broadening ($\Delta T_C=1.83$ K) compared to the reference sample ($\Delta T_C=1.10$ K) while $\Delta T_C$ is lower for samples from 2MG to 5MG and slightly higher for 6MG and 7MG. The sample 4MG has the lowest $\Delta T_C$ of 0.70 K.
Similar to the room temperature resistivity and the resistivity near transition, the change in phonon term resistivity ($\Delta \rho$) of the composites is also found to decrease with the increase in Mg metal fraction. The values of $\rho_{300}$ and $\rho_{40}$ reduce sharply from 32.82 $\mu\Omega$cm and 5.17 $\mu\Omega$cm to as low as 7.6 $\mu\Omega$cm and 0.28 $\mu\Omega$cm, respectively, as we go from the reference sample to 6MG. These observations are further supported by the values of RRR of the samples which increase with increase in Mg content. The connectivity factor, $A_F$ is also evaluated by the phonon term resistivity according to Rowell analysis [33] and is tabulated in table 5.2. Rowell connectivity analysis provides a means to estimate the fraction of the sample cross-sectional area that carries the current in the normal state. The analysis shows that the connectivity factor increases from 15.60% to 58.78% as we go from 1MG to 6MG whereas that for RMG is 15.55%.

Figure 5.5 shows optical images of polished surface of some of the Mg/MgB$_2$ composite samples. Figure 5.6 is a schematic representation of the microstructural evolution in the composites when excess Mg is used. On comparing the surface morphology of the composite samples, it can be seen that there is a gradual and distinct change in microstructure as we move from 1MG to 6MG. On increasing the Mg content, the amount of white tinted grains, characteristics of the unreacted Mg is found to be increasing from 1MG to 6MG as observed from the XRD results. The microstructure of the sample 1MG shows grey grain as the major matrix which decreases systematically with the addition of Mg. The grey matrix corresponds to the MgB$_2$ phase, the area of which diminishes with increase in Mg and evolves into thin layers surrounding the Mg grains in 6MG. The black spots which cover a large area in 1MG correspond to pores which are invariably present in all MgB$_2$ PIT wires prepared at normal conditions. Interestingly, the pores also come down significantly as we move from 1MG to 6MG.
Figure 5.5 Optical images of stoichiometric and excess Mg added samples (a) 1MG, (b) 2MG, (c) 4MG, (d) 6MG, (e) 7MG and (f) 6MG (zoomed view)

Based on the above microstructural information, a schematic representation of the microstructural evolution in the Mg/MgB$_2$ composites has been worked out as in figure 5.6. In Mg rich composites (2MG to 7MG), even though we use higher stoichiometric fractions of Mg compared to B, the amount of MgB$_2$ formed depends on the fraction of B available for the reaction. When the fraction of Mg increases, the fraction of MgB$_2$ formed decreases and when the Mg stoichiometry reaches around 6, the fraction of MgB$_2$ formed is minimal (13 wt%). The
lower reaction temperature and the deficiency of B make the reaction very slow and impel the formation of MgB₂ only on the surface of the unreacted Mg through solid state diffusion. The slow reaction rate also ensures the MgB₂ layers to be of high structural quality devoid of pores. Hence, it has been possible to develop Mg/MgB₂ composites wherein Mg remains as rounded metallic grains surrounded by thin and continuous layers of high quality MgB₂ superconductor. The stoichiometric fraction of Mg decides the thickness and continuity of the MgB₂ layers. In the present case, the sample 6MG has yielded the best properties in terms of the transport $J_C$ and hence this sample is considered to have the optimum composition under the heat treatment condition of 600 °C (5h). An important observation to be noted is that when wire samples with the composition of the 6MG is heat treated at 700 °C (2 h), the samples do not show superconductivity. This indicates the crucial role of selection of the heat treatment temperature vis-a-vis the composition for the development of the requisite microstructure.

Figure 5.6 Schematic representation of the composite formation.
The basic question of how a metal/superconductor composite with large metal fraction (89.1 wt% in 7MG) can exhibit superconductivity, can be answered in the light of the above discussion. The super current percolates through the MgB$_2$ layers formed around the Mg grains. Since the formation rate of the layers is extremely slow it is expected to have a much superior structure free from defects and pores. Moreover, the composites are found to be free of MgO, an insulator which obstructs the current. The connectivity factor of the composites also increases with the increase in Mg content because of the lower resistivity of Mg. The thinning down of the MgB$_2$ layers with the addition of more and more Mg helps to decrease the resistivity and increase the connectivity factor of the composites. Also as seen earlier the porosity in the system itself reduces drastically as the Mg content increases. These are presumed to be the main reasons for the steady increase of transport critical current density of the composites with increase in Mg content. Figure 5.7 shows comparison of typical transport properties for all stoichiometric and excess Mg added samples

Figure 5.7 Comparison of typical transport properties for all stoichiometric and excess Mg added samples
In summary, Mg/MgB₂ metal matrix composite superconductors with Mg content varying from 34.5 to 89.1 wt% have been developed by *in situ* solid state route at a relatively low temperature. The transport critical current density of all the composites is found to be higher than that of MgB₂ wires prepared under normal conditions. The $J_C$ is found to increase with increase in Mg content and attain a maximum at an Mg stoichiometry of 6. The $T_C$ of the composites is slightly lower than that of the reference sample while the $\Delta T_C$ even reduces in some cases. The microstructure of the samples exhibits a two-phase system containing metallic Mg and superconducting MgB₂. As the Mg content increases, MgB₂ evolves into continuous thin layers surrounding the Mg grains. The supercurrent percolate through these layers formed around the Mg grains. These layers are expected to be of high structural quality free from defects and pores. Similarly, the composite samples are free from MgO and the porosity is minimal. Moreover, the normal state transport properties and the overall grain connectivity of the composite wires increase steadily with the increase in Mg content. The above factors allow the composites to transport higher critical current which increases with increase in Mg content till an optimum thickness of the MgB₂ layers is reached. The finding is expected to have far reaching significance since the concept of a composite superconductor containing large fractions of metals is novel. Moreover, the optimized composite exhibits much higher critical current density than the superconductor prepared under normal conditions. The composite is inexpensive because of the simple process and cheap raw material (mainly Mg). The large fractions of Mg make the composite more ductile and this mitigates problems caused by brittle MgB₂ in the development of flexible superconducting wires for practical applications.

### 5.4 Conclusions

The effect of excess Mg on the structural and transport superconducting properties of Mg/MgB₂ composite wires, heat treated at lower temperatures is investigated and compared with normal MgB₂ samples. Even though MgB₂ phase is minimal in the two-phase
composite of metallic Mg and superconducting MgB₂, excellent transport $J_C$ is surprisingly observed in these wires. The metallic residual Mg existing in the sample significantly reduces the normal state resistivity of the composite and lower heat treatment temperature reduces current obstacles like MgO content and porosity due to volatile Mg loss. In a nutshell, the overall grain connectivity is improved in the system which simultaneously enhances the self-field critical current density. Besides this, the wire samples containing MgB₂ embedded Mg composite exhibits better ductility. This mitigates the problems caused by brittle MgB₂, improves mechanical workability and augments their potential for the development of monofilamentary and multifilamentary wires suitable for different applications.
References