Improvement of the critical current of \textit{in situ} Cu-sheathed MgB$_2$ wires by copper additions and toluene doping

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Abstract

Recent advances in the design of Cu-sheathed \textit{in situ} MgB$_2$ wires have shown promising results and made this kind of wire more competitive in terms of price to performance ratio in comparison to conductors with diffusion barriers made with metals inert to reaction with Mg. Recently reported additions of copper powder to the core of \textit{in situ} Cu-sheathed MgB$_2$ wires have shown that these additions can accelerate the formation of MgB$_2$, increasing its volume fraction and greatly decreasing the amount of Mg-Cu intermetallic phases present in the core after heat treatment. In this paper additional experimental results for toluene doping are reported and compared to wires with and without copper additions. All three wires were investigated by SEM, XRD and transport critical current measurements $J_c(B)$ at 4.2 K. The results showed that copper additions were effective in the whole measured field region, whereas toluene doping improved performance in the high field region.

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1. Introduction

The strong reaction between the copper sheath and magnesium in the core of \textit{in situ} MgB$_2$/Cu wires is a predominant factor limiting the critical current density, as was reported in the early work in the area \cite{1}. Nevertheless, thanks to the potential to achieve a high superconducting volume fraction, the engineering critical current density and low cost of such wires may still be attractive for some applications, including

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MRI. The use of a high heating rate during the heat treatment of such wires, which was originally suggested in [2] and investigated in detail in [3], proved to limit the MgCu 2 reaction layer thickness on the core-sheath interface [3], but it is not as effective as the recently reported copper powder additions to the in situ starting core material [4]. The reported increase in the MgB 2 volume fraction in the core and hence the critical current of such wires with added Cu was only slightly influenced by the Mg:B ratio in the starting powder, and was achieved after heat treatments with both slow and fast heating rates. Toluene doping has also recently been reported to cause an improvement in critical current with no degradation of current in the low field region [5]. However, the application of this method of toluene doping has not been reported in the literature for in situ MgB 2/Cu wires, in which the fraction of MgB 2 in the core after heat treatment is usually relatively low.

This paper reports such toluene doping and its influence on the phase composition and resulting critical current density of the core of in situ MgB 2/Cu wires. The investigation was carried out for both slow and fast heat treatments to assess the influence of heating rate on the wire performance. Two additional in situ MgB 2/Cu wires without toluene doping, but with and without copper addition to the core material, were also prepared and compared to the toluene doped wire.

2. Experimental procedure

The materials used in wire preparation were amorphous boron (99.99 %, -325 mesh), magnesium (99.8 %, -325 mesh), copper (99 %, -625 mesh), all from Alfa Aesar, and toluene (99.8 % C 6H5CH3, anhydrous) from Sigma-Aldrich. The toluene doping was performed by mixing 1.5 ml of toluene and 0.5 g of boron for 1 h in an Ar atmosphere, and then vacuum drying at 155 °C for 3 h. This procedure is expected to give 0.4 wt.% of carbon doping to boron by toluene decomposition [5]. Powder mixtures for the cores of the wires, with the Mg:B ratio of stoichiometric MgB 2, were prepared using a pestle and mortar in an Ar atmosphere. The toluene doped sample (T) was prepared using the boron powder processed with toluene; the other two compositions (Table 1) were prepared using fresh boron, with the addition of 3 at. % of Cu powder for the Cu added wire (C). The powder mixtures were packed under an Ar atmosphere into Cu tubes with internal and external diameters of 2.1 mm and 3 mm respectively. Wires were cold drawn to 1.02 mm in 23 steps with an average cross-sectional area reduction of 9 % per pass.

Two heating ramp rates of 150 °C min -1 (fast ramp) and 20 °C min -1 (slow ramp) were used for heat treatments of 5 cm long wires in a flowing 95 % Ar + 5 % H protective atmosphere at 700 °C with a 5 min dwell. Samples were left to cool naturally to room temperature in the furnace.

<table>
<thead>
<tr>
<th>Wire label</th>
<th>Composition of the core powder</th>
<th>Sheath material</th>
<th>Core volume fraction [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>Mg+2B</td>
<td>Cu</td>
<td>40</td>
</tr>
<tr>
<td>C</td>
<td>Mg+2B+0.03Cu</td>
<td>Cu</td>
<td>40</td>
</tr>
<tr>
<td>T</td>
<td>Mg+2B+toluene</td>
<td>Cu</td>
<td>40</td>
</tr>
</tbody>
</table>

The samples were prepared by polishing for examination in a Camscan MX2600 FEG-SEM operating at an accelerating voltage of 10 kV in back-scattered electron (BSE) imaging mode.

Powder X-ray Diffraction (XRD) scans were performed using a Bruker D8 Advance diffractometer in the Bragg-Brentano configuration with CuKα1 irradiation at a 2θ scan rate of 2° min -1 in the range 18-85°. Powder samples were extracted from 32 mm long wire samples after opening each wire by cutting along
the wire axis. The data were analysed with HighScore Plus software (PANalytical B.V.). Rietveld refinement was performed on data in a $2\theta$ range from 34.5° to 85° and using structural models of MgB$_2$, Mg-Cu, MgCu$_2$, MgO and Cu. The goodness of fit of the refined patterns ranged from 1.28 % to 1.93 %.

Transport critical current measurements were performed in the ILHMFLT in Wroclaw, Poland using a four point method on straight 18 mm long samples in a liquid helium bath and in the bore of a Bitter electromagnet (type Bitter 100, BM1 [6]), perpendicular to the magnetic field. Measurements were performed at constant field while ramping the current (up to 150 A). The critical currents $I_c$ were obtained by applying an $E_c=1 \mu$V cm$^{-1}$ electric field criterion to the measured $E$-$I$ curves. The $n$ values were obtained by fitting the curve $E=E_c(I/I_c)^n$ to the measured data with the Levenberg-Marquardt method in the range of electric field from 1 $\mu$V cm$^{-1}$ to 10 $\mu$V cm$^{-1}$.

3. Results and discussion

SEM was performed on the cross-sections of samples (table 1) after heat treatment for 5 min at 700 °C with a ramp rate of 20 °C min$^{-1}$ (figure 1). The microstructure of the core of the wires is distinctly different for pure sample P and toluene doped sample T in comparison with sample C with added copper. Wires P and T (figure 1 (a) and (c)) have long-range inhomogeneity, with several distinct regions of dark contrast found by EDS to have high boron content. In those wires, MgCu$_2$ is clustered in non-uniformly distributed regions, whereas wire C with added copper contained a finer and more uniform mixture of MgB$_2$ and MgCu$_2$ (figure 1 (b)).

To assess the wire core compositions after heat treatment, X-ray powder diffraction was performed on powder from the cores with all compositions (Table 1) and after heat treatment with both heating rates.

Unreacted amorphous boron remaining in the samples could not be detected by our XRD measurements, but mass fractions of the detected phases obtained from Rietveld refinement were corrected based on the stoichiometric Mg and B ratio in the starting powders (Table 1). The corrected mass fractions of each phase were then converted to vol. % and are presented in Figure 2. The total
volume (100%) in this case refers to the total volume of material in each wire core, excluding any porosity, and therefore does not correspond to the total geometrical core volume.

In Figure 2 (a) it can be seen that the highest MgB$_2$ fractions (>65 vol. %) are achieved in the wire with added Cu (C) and those fractions are very little affected by heating rate. In contrast, the fraction of MgB$_2$ in the pure wire (P) is much higher for the slower heating rate (~10 vol. % difference). The toluene doped wire (T) has the lowest MgB$_2$ fraction in the core, but it is only slightly affected by the heating rate. This low (<50 vol. %) fraction of MgB$_2$ might suggest a reduction in the reactivity of boron due to the toluene doping procedure (see section 2). The fractions of MgCu$_2$ (Figure 2(b)) in the core have similar but inverted trend to the MgB$_2$ fractions in all wires. After heat treatment, the fractions of Mg$_2$Cu and the Cu-rich Mg-Cu solid solution (‘Cu’) in the core material are very low (<1.5 vol. %) (Figure 2 (c)).

The fractions of MgO and B are lowest for samples with added copper (C) and higher for pure (P) and toluene doped samples (T) (Figure 2 (d)), but this might be because of the presence of unreacted Mg, which was present after heat treatment and later oxidized during XRD measurement.

For wires P and C, the critical current (Figure 3 (a)) is correlated with the volume fraction obtained from XRD (Figure 2 (a)). Only a very small difference in critical current and the volume fraction of MgB$_2$ was measured between the samples of the wire with Cu additions (C) produced at the two heating rates, whereas for the pure wire (P) the higher volume fraction of MgB$_2$ for a slow heating rate is reflected in a higher critical current. The relative insensitivity of the critical current of wire C to heating rate, which is...
potentially convenient for production, is a result of the increased rate of MgB₂ formation. The slope of the critical current vs. magnetic field curve is changed for the toluene doped wire (T), but only for a slow heating rate (20 °C min⁻¹, Figure 3 (a)). Fast heating rate heat treatment of the toluene doped wire (T) resulted in no change in critical current behavior in comparison to pure wire (P) reacted in the same conditions. Such fast and short heat treatment conditions seem to hinder the carbon substitution process into the MgB₂ crystal structure in the strongly reactive Mg-Cu system of MgB₂/Cu wires.

The steepness of the superconducting transitions is also influenced by the core starting composition and heating rate, and is represented as an n-value plotted vs. magnetic field in Figure 3 (b). The decrease in n-value with increasing magnetic field is similar for all samples, but the values are much higher at all fields for the wire with added Cu (C). This behaviour is probably related to the greater uniformity of the core for these wires (as shown in figure 1 (b)) [4].

4. Conclusions

Two interesting ways of improving the critical current of in situ MgB₂/Cu wires are presented in this short paper. The critical currents of these wires are found to be higher after slow ramp heat treatment, and were doubled in the whole field range by copper additions (3 at. %) and almost tripled by toluene doping in the field region above 5 T. Further work will involve combining these two approaches and checking if the copper addition and toluene doping can have an additive effect on critical current.

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References