Carbon doping of precursor boron powder for control of normal resistance of MgB$_2$ bulks for specific use in fault current limiter applications

J Archer and A L L Jarvis*

School of Engineering, University of KwaZulu-Natal, King George V Ave, Durban, KwaZulu-Natal, 4014, South Africa

Jarvis@ukzn.ac.za

Abstract. Magnesium Diboride (MgB$_2$) bulk superconductor has been manufactured in order to study the enhancement of the normal resistivity for application to superconducting fault current limiters (SFCLs). SFCLs have proven to be a viable means for limiting surge currents by dissipating fault energy as the superconductor quenches. As the current limiting behaviour is determined by the normal resistivity ($\rho_n$), research has been conducted to evaluate an effective means to increase $\rho_n$ for bulk superconducting MgB$_2$, which is intrinsically much lower than for high temperature superconductors. Intragranular carbon doping has been confirmed as a means to increase $\rho_n$, and was implemented by chemical vapour deposition (CVD) on the boron precursor powder by ethylene gas at 600 ºC for durations up to 6 hours in a tubular furnace apparatus. In situ manufacturing of MgB$_2$ bulk was performed using the reactive liquid magnesium infiltration technique. Overall, carbon doping provided a factor of 11.00 increase in the residual resistivity, $\rho_0$, which provides the initial limiting action to fault currents, for an accompanying decrease in the critical temperature, $T_c$, of 2 K.

1. Introduction

Globally, as power demand grows and the use of renewable energy sources increase, it is typically met with an increase in grid complexity and distributed generation, which increases fault current levels and makes them harder to predict [1]. The installed switchgear capacity may no longer be sufficient to support this growth, presenting a need for fault current limiter to reduce the magnitude of fault currents before switchgear interruption [2].

In a resistive SFCL under fault conditions, the superconductor quenches and presents to the grid an impedance determined by the normal-state resistivity, $\rho_n$, dissipating fault energy through resistive losses (joule heating), thus limiting the fault current. Once the fault has been cleared, the FCL can be ‘reset’ by cooling the superconductor to superconducting state again.

Since it is $\rho_n$ that determines the energy dissipated during fault currents, a high $\rho_n$ is desired for enhanced current limiting properties. A practical problem with the use of MgB$_2$ in resistive SFCLs is the intrinsically low normal resistivity of MgB$_2$, resulting in longer lengths of superconductor required, increasing both size and cost. Work has been done to investigate the effect of chemical doping on the superconducting properties of MgB$_2$, primarily in the form of $J_c$ and upper critical field, $H_{c2}$, and has revealed increases in these parameters up to a certain limit with an increase in disorder due to doping [3]. The approach taken in this research has been to further dope the specimens to
substantially increase $\rho_n$, making it more suitable for use in FCLs whilst still maintaining reasonable operational conditions.

2. Experimental procedure

2.1. Carbon Doping

MgB$_2$ specimens were prepared by the reactive liquid infiltration technique, with the precursor boron powder doped by carbon chemical vapour deposition using ethylene gas. For the chemical vapour deposition (CVD) of carbon to the boron precursor powder (Sigma-Aldrich, 95-97%, amorphous, submicron particle size), a purpose-built stainless steel tubular furnace assembly was used in conjunction with the gaseous hydrocarbon ethylene ($C_2H_4$) as the carbon source. The ethylene gas was introduced to a relative pressure of 80 kPa. The ethylene in the tube was flushed hourly at the 600 ºC operating temperature for a total doping period of 6 hours, to obtain high doping concentrations up to 16%. Estimation of the carbon content was achieved by measurement of the boron precursor powder mass before and after CVD with a Mettler Toledo PB3002-S.

2.2. Reactive Liquid Infiltration

Specimens were manufactured by the reactive liquid infiltration (RLI) technique [4] in appropriately designed stainless steel containers. A number of iterations on the designs were made, to improve various aspects; straightforward removal of product, simplified welding of crucibles, increasing internal reaction pressure, and minimising stainless steel volume and machining time.

Five bulk specimens of MgB$_2$ were produced representing carbon doped boron concentrations from 0-16%. Optical and scanning electron microscopy analysis was performed on the specimens, revealing good density. The samples were sectioned by diamond wafering blade into thin rectangular slices for resistive testing and into rectangular bars for AC susceptibility investigations.

2.3. DC resistivity measurements

DC resistivity measurements were performed on all of the samples with a 4-wire apparatus constructed with gold-plated spring-loaded test pins. This facilitated rapid changing of the samples, and the internal springs ensured electrical contact with the sample despite differing in thermal expansion coefficients in apparatus, and achieved reproducibility after unload-reload cycles. The sample stage was cooled by a two stage GM cryocooler with a Lakeshore 336 temperature controller.

2.4. AC susceptibility

The bar sections were inserted into an AC susceptibility apparatus, to provide contactless measurement of the critical temperature. This was required because the apparatus used for DC resistivity measurements with the limited equipment specifications introduced unavoidable thermal heat leakage, and particularly, joule heating in the sample contacts. This introduced uncertainty into the critical temperatures obtained, so a contactless approach was taken.

3. Results and Discussion

3.1. Sample morphology

Scanning electron microscopy (SEM) was used to investigate the topology of the surface presented after abrasion cutting, enabling some intragranular views as well as some of the intergranular interfaces, the grain boundaries. A scanning electron micrograph is shown in figure 1, and a low magnification optical micrograph is shown in figure 2.
Smaller grains appeared to be about 100 nm in diameter throughout all the micrographs, thus doping did not appear to affect the grain size. Optical microscopy showed a well-formed MgB$_2$ phase with few voids, and clear bimodal grain distribution, likely as a result of bimodality in the precursor boron powder [5].

3.2. DC resistivity results

The resistivity results are shown in figure 3, showing a distinct increase in resistivity with an increase in carbon content, with further analysis of the data shown in figure 4, where the overall resistivity has been broken down into the residual and phonon-contributed resistivities. The separation is in accordance with the Rowell criterion [6], with the phonon contribution, $\Delta \rho$, defined as the difference between room temperature resistivity, $\rho_{300K}$, and the resistivity just above $T_c$.

Carbon doping appeared to increase both the residual resistivity as well as the phonon-contributed resistivity, implying that the doping had also decreased the intergranular connectivity. Data from each specimen was thus divided by the geometrical factor, $A$, which was defined as the specimen’s phonon contributed resistivity, $\Delta \rho$, divided by the single crystal phonon contribution, $\Delta \rho_{SC}$, of 10 $\mu\Omega$.cm. After this treatment, a clear increase in the residual resistivity as a function of doping could be observed.

**Figure 1.** SEM micrograph of an undoped specimen (~100 000 ×).

**Figure 2.** Optical micrograph showing clear bimodal grain distribution.

**Figure 3.** Resistivities of doped specimens as a function of temperature, showing superconducting transitions.

**Figure 4.** Resistivity contributions from residual and phonon components for the doped specimens, after division by the respective geometrical factors.
3.3. AC susceptibility results

The critical temperatures characterised by AC susceptibility are shown in figure 5, showing only a small overall change in $T_c$, and are presented in figure 6 with the corresponding normalised resistivity. Without any secondary peaks in the AC susceptibility data, the inter-granular doping that was responsible for the decrease in effective cross sectional area in the resistivity measurements was not observed in the specimens, with the exception of the 8% doped specimen.

![AC susceptibility results](image)

**Figure 5.** Real susceptibility of specimens doped in the range of 0% to 16%.

**Figure 6.** Critical temperature dependence on the normalised resistivity. The solid line represents a linear fit applied to the data.

4. Conclusions

A study of the effect of carbon doping on MgB$_2$ specimens fabricated via the RLI technique was performed, with the research goal being to increase the normal state resistivity of MgB$_2$ by the use of carbon doping, particularly to establish if the resistivity could be increased significantly whilst still maintaining reasonable operational requirements.

Boron powder was doped by chemical vapour deposition of carbon, before use in the reactive liquid infiltration technique. Morphology analysis performed by SEM and optical microscopy revealed that all specimens were dense, featuring few voids, and no signs of impurity phases. There was a clear bimodal grain distribution, and doping did not appear to affect the grain size.

The DC resistivity was measured, and AC susceptibility was used to determine critical temperature. Analysis of resistivity measurements established that doping increased the normal state resistivity, via both increases in the residual resistivity, and phonon-contributed resistivity. Even when the geometrical factor was taken into account, the resistivities increased as a function of doping. From the results of the AC susceptibility measurements, clear transitions were evident, and the critical temperature was defined from these low-field measurements.

Overall, carbon doping provided a factor of 11.00 increase in $\rho_0$, which provides the initial limiting action to fault currents, for an accompanying decrease in the critical temperature, $T_c$, of 2 K.

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