Strong influence of boron precursor powder on the critical current density of MgB$_2$

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Abstract
The influence of the nature of the boron precursor on the superconducting properties of polycrystalline MgB$_2$ was studied. Critical current densities ($J_c$) for MgB$_2$ made from high purity amorphous boron are at least a factor of three higher than typical values measured for standard MgB$_2$ samples made from amorphous precursors. Two possible mechanisms are proposed to account for this difference.

Samples made from crystalline boron powders have around an order of magnitude lower $J_c$ compared to those made from amorphous precursors. X-ray, $T_c$ and resistivity studies indicate that this is as a result of reduced current cross-section due to the formation of (Mg)B–O phases. The samples made from amorphous B contain far fewer Mg(B)–O phases than crystalline B despite the fact that the amorphous B contains more B$_2$O$_3$. The different reactivity rates of the precursor powders accounts for this anomaly.

1. Introduction
Recently, there has been a considerable amount of research undertaken in order to understand the influence of dopants and nanoparticle additions to enhancing the $J_c$ of the MgB$_2$ [1–5]. However, before understanding how these additions influence $J_c$, it is important to understand how intrinsic impurities in MgB$_2$ (in particular oxides of Mg and B constituents, and Mg stoichiometry) enhance or degrade $J_c$. There has been much discussion of the difference between ‘clean’ and ‘dirty’ ‘undoped’ samples, and about difficulties in relating sample resistivity to $T_c$ and $J_c$. Clearly, there are many factors involved, including reduction of current-carrying cross-section as a result of intergrain second phases, formation of grain boundary Josephson junctions by grain boundary phases, intragrain scattering as a result of poorly controlled stoichiometry (e.g. Mg vacancies, oxygen substitution, or possibly even B vacancies), or scattering from intragrain nanoscale precipitates [6, 7]. Control of these scattering mechanisms is at an early stage and is key for understanding the extent to which doping of intragranular regions (e.g. with C) may also unintentionally produce deleterious intergrain second phases.

The aim of this study is to understand how the $J_c$ versus field behaviour for MgB$_2$ is influenced by the form and purity of the boron precursor. In addition to the scientific interest of the work, the study has considerable merit from the application point of view.

2. Experimental details
MgB$_2$ samples were prepared by reacting Mg and B using conventional solid state reaction. Crystalline magnesium powder (Alfa Aesar, 99.8%, 325 mesh) and four different types of boron powder (two different purities of both crystalline B and amorphous B), as shown in table 1, were used. Mg and B were mixed in the stoichiometric ratio of 1:2, followed by grinding for 1 h. The resultant mixture was then pressed into pellets of 5 mm in diameter and about 2 mm thick using a hydraulic press with an applied load of 2 tonnes. The pellets and approximately the same weight fraction of Mg curls (~0.003 g per 0.030 g ‘Mg + 2B’) were wrapped in Ta foil, placed inside a tubular furnace and annealed at 900 °C for 15 min in a reducing atmosphere of 2% H$_2$–Ar. The heating and cooling rates used were 15 °C min$^{-1}$. Several different samples were made in separate reaction runs to check for reproducibility.
Table 1. Source, form and purity of the different boron powders with their particle size distribution.

| Boron powder | Source      | Form       | Purity (%) | Peak value(s) of particle size distribution ($\mu$m)          |
|--------------|-------------|------------|------------|--------------------------------------------------------------|
| B-C98        | Alfa Aesar  | Crystalline| 98         | 21.10 [325 mesh]$^b$                                       |
| B-C99$^a$    | FluoroChem  | Crystalline| 99         | 11.42, 0.56 [<40 $\mu$m]$^b$                               |
| B-A9597$^a$  | Fluka       | Amorphous  | 95–97      | 0.56, 2.42 [–]$^b$                                         |
| B-A9999      | Alfa Aesar  | Amorphous  | 99.99      | 0.54 [325 mesh]$^b$                                         |

$^a$ Powders with dual particle size distribution.

$^b$ Particle size as indicated in the chemical label.

X-ray diffraction (XRD) spectra in the $\theta$–2$\theta$ step-scanning mode with 0.05$^o$ increments were recorded in a Philips PW1050 diffractometer with a Cu Kα radiation source. Room-temperature resistivity was measured using a standard four-probe technique. In order to eliminate the effect of Mg which had condensed on the surface of some of the pellets during annealing, each sample was polished before the measurement. The superconducting transition temperature, $T_c$, was obtained using a commercial Quantum Design DC magnetic properties measurement system (MPMS) by first cooling the sample in zero field and then measuring the magnetic moment as the sample was warmed in field. Magnetization hysteresis loops were performed on bar-shaped samples of $\sim$2 mm$^3$ volume with the magnetic field applied parallel to the longest dimension of the sample. Magnetic critical current density was estimated based on the critical state model [8].

Particle size distribution was determined using a Mastersizer E particle size analyser from Malvern Instruments. To ensure reliable data acquisition, 0.05 g of boron powder was ultrasonically dispersed in acetone to avoid agglomeration of powder particles. The equipment was calibrated each time before the subsequent measurement to reduce the background spectrum.

3. Results and discussion

Figure 1 shows the x-ray diffractogram for the crystalline boron (figure 1(a)) and amorphous boron powders (figure 1(b)). The patterns can be indexed according to single-phase boron, except for the $B_2O_3$ peaks indicated with dashed lines. There is also an unidentified peak at around 18.4$^o$. It is difficult to quantify the differences in the amount of $B_2O_3$ between the different forms of B’s, e.g. the $B_2O_3$ peaks appear high in the amorphous boron powder (B-A9999) but this is set against the low-intensity amorphous B features. Nevertheless, it is expected that the amorphous powders contain more $B_2O_3$ since they are fabricated by high-temperature Mg reduction of $B_2O_3$. It is interesting that the B-A9597 powder shows some crystalline peaks from B, despite being labelled as amorphous.

The crystalline B is expected to contain fewer oxygen impurities since it is formed by high-temperature reduction of halides of B with H$_2$ gas. For the amorphous boron, the difference between different purity powders relates to the amount of excess Mg present as a result of the reduction.

X-ray diffractograms of the MgB$_2$ pellets made from the corresponding B precursor powders are shown in figure 2. MgO was present as a second phase in measurable quantities in all the MgB$_2$ samples, although it has the smallest fraction in the purest amorphous B precursor sample, A9999. The samples formed from the amorphous powders showed only the presence of MgO as a second phase.

The impurities in the crystalline (C) precursor samples consisted of boron oxides and magnesium boron oxides. In addition, several peaks due to unidentified phases were clearly observed, and are marked with circles. Some unreacted Mg was also found in sample C98 (an excess of Mg was always found in the different samples made from the B-C98 batch).

Summarizing the x-ray data, more (Mg)B$_2$O$_y$ impurity phases were formed in samples prepared from the crystalline rather than amorphous boron. At first, this finding seems surprising considering that the crystalline B precursor powders are expected to contain less oxygen, and that they contained less $B_2O_3$ than the amorphous powders (figure 1). The results can be explained based on the reactivity of the powders. Table 1 shows that the crystalline boron contains large particles of tens of microns in size, whereas the amorphous powders have particle sizes of $\sim$0.5 $\mu$m. The reactivity of the amorphous...
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Table 2. Room-temperature resistivity, density, relative strain and cell parameters of samples prepared from different boron powders.

| Sample | Pellet 1 | Pellet 2 | Density (g cm⁻³) | Strain (%) | a (Å) | c (Å) |
|--------|---------|---------|------------------|------------|-------|-------|
| C98    | 274.8   | 344.1   | 1.48             | 0.171 ± 0.043 | 3.0826 ± 0.0007 | 3.520 ± 0.001 |
| C99    | 242.6   | 230.3   | 1.45             | 0.188 ± 0.046 | 3.0820 ± 0.0010 | 3.524 ± 0.002 |
| A9597  | 44.6    | 60.7    | 1.16             | 0.211 ± 0.031 | 3.0789 ± 0.0006 | 3.521 ± 0.001 |
| A9999  | 178.4   | 225.3   | 1.23             | 0.198 ± 0.019 | 3.0822 ± 0.0005 | 3.525 ± 0.001 |

Figure 2. X-ray powder diffraction patterns of MgB2 samples made from different B powders. The unlabelled peaks are MgB2.

powders is much greater than that of the crystalline powders, and the reduced particle size further enhances the reaction rate [9]. Hence, when the crystalline B powders come into contact with surface oxidized Mg powder, the reaction to form MgB2 is relatively slow and there is sufficient time for (Mg)BxOy phases to form. On the other hand, for the amorphous powder, the Mg reacts rapidly with B to form MgB2 and with B2O3 to form MgO + B. Longer annealing time led to the formation of more Mg(BxOy) and B2O3 phases in the crystalline precursor samples, but not for the amorphous ones.

Table 2 lists the lattice strain estimated from the Williamson–Hall plot [10]. The peak breadth and 2θ-values were refined and carefully checked to avoid overlapping from impurity phases. Comparison of the experimental data with a Si standard also showed that size broadening effects were small. Within the error of calculation, there was no significant difference in relative strain amongst samples and there was no evidence of anisotropic strain. The cell parameters were calculated using the Rietveld method in the approximation of a pseudo-Voigt function by taking into account the contribution from thermal displacement of atoms. The hexagonal crystal structure of MgB2 [11] was used as the reference data and the MgO phase was included in the refinement. The a-axis for A9597 was the smallest amongst the samples while the parameter did not change to within error. Small a values have previously been related to intergranular strain effects [12] and

this possibility is discussed for sample A9597 in relation to the observed microstructure. Nevertheless, the very small differences in a between samples indicates that there are no significant structural perturbations within the crystalites.

Typical SEM images of the four different samples are shown in figure 3. The larger size of the grains of the crystalline samples (a few hundred nanometres) compared to the amorphous samples (~100 nm and less) is consistent with the measured sizes of the precursor boron powders of table 1. In addition, the bimodal particle sizes observed in the B-C99 and B-A9597 boron precursor powders (table 1) are also reflected in bimodal grain sizes in the resulting MgB2 samples, particularly for the A9597 sample. This strong bimodality in A9597 likely leads to greater intergranular strain, and thus accounts for smaller a. The A9999 sample has the finest and most uniform grain size.

Figure 4 shows the superconducting transition temperature measured at 20 Oe. Tc was determined by taking the first deviation point from linearity that signifies the transition from the normal to superconducting state. The Tc-values were in the range 37.9 K (C99) to 38.8 K (C98). Both A9597 and A9999 showed the same Tc of 38.2 K. Our results are in contrast to those of Ribeiro et al who found that Tc is improved with boron purity [13]. The breadth of the Tc transitions are larger for the crystalline precursor samples than for the amorphous precursor samples (i.e. 2–3 K compared to 0.75–1 K, respectively, using a 10–90% criterion), suggestive of greater sample inhomogeneity and/or poorer intergrain connectivity for the crystalline precursor samples.
significant amount of oxide impurities (B). Temperature resistivity values were high resistivities were also measured in our samples, as the lower densities (table 2) than for the crystalline precursor samples. However, the values reported were lower than in this study, for example by a factor of 4–5 at 20 K, 3 T. As far as is known, the only other report of similar high $J_c$ values to those reported here in MgB$_2$ made using similar high purity amorphous boron [7]. Despite the high purities of the precursors, the samples were believed to be rather ‘dirty’ because room-temperature resistivity values were ~180 $\mu\Omega \text{cm}$ [7]. Similar high resistivities were also measured in our samples, as discussed below.

The highest $J_c$ of all the samples was achieved in sample A9999 prepared using the highest purity boron. Zhou et al. previously showed that samples made from different purity amorphous borons exhibited different $J_c$, and also that the highest purity boron (99.99%) yielded the highest $J_c$ [14]. However, the values reported were lower than in this study, for example by a factor of 4–5 at 20 K, 3 T. As far as is known, the only other report of similar high $J_c(H)$ values to those reported here in MgB$_2$ made using similar high purity amorphous boron [7]. Despite the high purities of the precursors, the samples were believed to be rather ‘dirty’ because room-temperature resistivity values were ~180 $\mu\Omega \text{cm}$ [7]. Similar high resistivities were also measured in our samples, as discussed below.

Figure 4. Temperature dependence of normalized susceptibility. Inset: transition temperature in a wider temperature range.

Figure 5 compares the field dependence of $J_c$ up to 5 T. The form of $J_c(H)$ was identical and $J_c$ values were reproducible within 25% for the same precursors from one sample batch to the next. Higher $J_c$ values are achieved for the amorphous precursor samples, despite the lower densities (table 2) than for the crystalline precursor samples.

Both at 6 and 20 K, $J_c(H)$ of A9999 is an order of magnitude larger than C99. C98 has the lowest $J_c$ of all the samples and $J_c$ decreased rapidly with $H$, again suggestive of poor intergrain connectivity for the crystalline samples. The $J_c(H)$ data are consistent with the x-ray data (figure 2), namely, that the crystalline precursor samples contained a significant amount of oxide impurities (B, O, Mg–B–O, and MgO) whereas the amorphous precursor samples contained only MgO.

The high resistivity values for the crystalline precursor samples (~230–340 $\mu\Omega \text{cm}$) suggest that the oxide phases decrease the current-carrying cross-section by obstructing some of the intragrain regions. From XRD, the main difference between C98 and C99 is the presence of Mg in C98, as well as a larger amount of MgO. The fact that the resistivities for C98 are only marginally higher than for C99 (table 2) suggests a combined effect of a decrease in resistivity due to the presence of extra Mg, but also an increase due to extra MgO, some of which may come from a surface oxide layer on the Mg which is small in volume fraction (hence it does now show up strongly in the x-ray spectra) but large in surface area (hence leading to an increase in the resistivity).

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Considering that the A9999 samples showed similar x-ray diffraction patterns to the A9597 samples, except for a slightly larger fraction of MgO in A9597, it might be expected that the $J_c$-values would be similar, and not a factor of 3 or more higher. The room-temperature resistivity (~50 $\mu\Omega \text{cm}$) of A9597 is typical for a clean MgB$_2$ sample and is around a factor of 5 lower than the crystalline precursor samples which contained several impurity phases. Surprisingly, the ‘clean’ A9999 samples which were also expected to have resistivities of ~50 $\mu\Omega \text{cm}$ or lower, similar to the A9597 samples, had high resistivities of ~200 $\mu\Omega \text{cm}$, approaching the crystalline precursor samples. It is possible that these resistivity values were artificially high because the samples were brittle and sometimes cracked when contacts were applied to them—the reason for the brittleness can be attributed to the uniform, fine grain structure as shown in figure 3(d), but this would not explain the higher $J_c$ values of the A9999 samples. Two other possible reasons for the higher resistivities are:

(a) larger grain boundary contribution to resistivity because of the very fine grain size, or
(b) possible presence of Mg non-stoichiometry in the MgB$_2$ grains at a level insufficient to cause a degradation of $T_c$.

In the former scenario, the $J_c$ enhancement in the A9999 samples would be by additional grain boundary pinning, and in the latter scenario $H_{c2}$ would be increased by enhanced intragrain scattering. Since the $J_c(H)$ behaviour for the A9999 samples is, in fact, better than some previously reported doped samples [15], whatever is causing the significant enhancement in $J_c$ over normal amorphous precursor MgB$_2$ samples requires further investigation. In this way, a clear understanding of the factors that influence superconducting properties of parent ‘undoped’ MgB$_2$ will enable a better understanding of how doping also influences superconducting properties (e.g. connectivity, intragrain and intergrain scattering).

4. Conclusions

In conclusion, we have shown that the form and purity of boron precursors are of critical importance to the $J_c(H)$ behaviour of MgB$_2$ samples. The $J_c(H)$ behaviour of the samples made from the crystalline boron precursors can be explained in
terms of a reduced effective cross-sectional area as a result of the presence of several oxide impurities. The differences between amorphous boron powders are less clear, with very large differences in $J_c(H)$ obtained from samples showing very similar phase purities. Nevertheless, it is clear that to obtain reproducible $J_c$ values, very careful control of amorphous B starting powders and reaction conditions are required.

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