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Effect of the sintering temperature on the microstructure and superconducting properties of MgB₂ bulks manufactured by the field assisted sintering technique

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Abstract
Magnesium diboride (MgB₂) bulk superconductors may have practical applications as permanent magnets owing to their ability to trap larger fields than conventional ferromagnets and a transition temperature of 39 K that make them attractive for use in cryogen-free systems. Unlike the cuprate high temperature superconductors, grain boundaries in MgB₂ act as pinning sites not weak links, and so show good current carrying ability in polycrystalline samples. This enables the materials to be processed using standard ceramic processing methods which are scalable to large diameters and mass production. The maximum trapped field in bulk superconductors scales with the critical current density (Jc) of the material as well as the radius of the sample. To obtain the highest possible Jc values in MgB₂ at high fields requires the bulk materials to be fully dense but fine-grained material, and possibly with a nano-scale distribution of non-superconducting impurity particles to further enhance pinning. Field assisted sintering technology (FAST) is a rapid process for obtaining dense ceramics from materials like MgB₂ which are difficult to sinter with conventional pressure-less techniques. Rapid heat treatments are attractive both from a manufacturing point of view and because the total time that the sample is held at high temperature is short, limiting grain coarsening. In this paper, we report a systematic study of the influence of processing temperature on microstructure and superconducting properties of MgB₂ bulks manufactured using FAST. We conclude that processing temperatures above 1000 °C are required to obtain materials that have sufficiently high electrical connectivity to generate large magnetic moments. However, the intrinsic (intragrain) Jc values in MgB₂ are better in the samples processed at 900 °C owing to their finer scale microstructures and the MgB₂ lattice being more defective.

Supplementary material for this article is available online

Keywords: MgB₂, field assisted sintering, processing temperature, microstructure, superconducting magnet, spark plasma sintering, connectivity

(Some figures may appear in colour only in the online journal)

1. Introduction

Since the discovery of superconductivity in MgB₂ in 2001 [1] it has been recognised as a promising material for practical applications owing to its relatively high critical temperature...
(\(T_c\)) and the fact that MgB\(_2\) can be processed easily by scalable and readily available powder routes [2]. The \(T_c\) of MgB\(_2\), 39 K, is the highest of any binary compound which makes it more suitable for helium-free applications than conventional low temperature superconductors (LTS) such as NbTi and Nb\(_3\)Sn.

MgB\(_2\) has been successfully produced in various forms including wires, tapes and bulks using \textit{in situ} and \textit{ex situ} methods. The \textit{ex situ} processing route, in which pre-synthesised MgB\(_2\) powder is consolidated at high temperature usually with the assistance of pressure, can produce artifacts with significantly higher density than can be achieved by \textit{in situ} reaction of Mg and B powders. This is because the formation of MgB\(_2\) from Mg and B precursor powders is accompanied by a large increase in theoretical density from 2.10 g cm\(^{-3}\) for the powder mixture to 2.63 g cm\(^{-3}\) for the MgB\(_2\) phase, leading to a maximum relative density of 80\%, assuming full densification during the \textit{in situ} process [3]. On the other hand, \textit{ex situ} MgB\(_2\) samples with a relative density above 95\% have been produced by several research teams using the field assisted sintering technique (FAST) also called spark plasma sintering (SPS) [3–7] or ultra-high pressure methods [8]. FAST is a very effective technique for sintering a broad range of materials, including those that cannot be densified using conventional pressureless sintering [9–11]. Consequently, FAST has been adopted by several research groups to investigate the effect of sintering parameters such as the pressure, dwell time and heating rate on the microstructure and superconducting properties of MgB\(_2\) bulk specimens. Dancer et al [3] found that higher pressures led to an increase in density and suggested that the pressure does not have a significant effect on the critical current density (\(J_c\)) for samples with a relative density above 90\%. Aldica et al [7] have shown that the dwell time had only a small influence on the relative density or \(J_c\). In another study [6] they found that the heating rate had a small effect on the impurity content of the consolidated samples but did not observe a clear trend for \(J_c\).

Despite the significant influence of processing temperature on the properties of sintered materials, only very few studies have investigated its effect on the microstructure and superconducting properties of MgB\(_2\) bulk specimens. Shim et al [5] sintered MgB\(_2\) powder at temperatures ranging from 900 °C to 1050 °C using FAST, and they observed an increase in the relative density of the specimens with processing temperature, going from 78\% up to 99\% for the samples sintered at 900 °C and 1050 °C respectively. Habler et al [12] consolidated MgB\(_2\) powder at temperatures between 850 °C and 950 °C using FAST. They found that the MgO and MgB\(_4\) content in the bulk samples increased with higher processing temperatures. They also observed that the sample sintered at 950 °C showed the highest irreversibility field (\(B_{irr}\)). The trapped field performance of real MgB\(_2\) bulk samples depends on their internal microstructure in a complex way through a combination of extrinsic and intrinsic effects [13]. Extrinsic factors, including reduced volume fraction of the superconducting phase and poorly conducting interfaces between grains/particles, lead to the actual cross-sectional area for current transport being lower than the geometric cross-sectional area of the sample, and intrinsic factors influence the local microscopic \(J_c\) values of the superconductor within the grains or particles themselves.

Here we report a detailed and systematic study of the effects of processing temperature on the microstructure and superconducting properties of \textit{ex situ} MgB\(_2\) bulk samples manufactured by FAST over a wide range of temperature, with the aim of understanding the interplay between intrinsic and extrinsic effects that will influence their ultimate trapped field performances.

2. Experimental details

Pre-synthesised MgB\(_2\) (purity: 99\%, Alfa Aesar) was poured into a 20 mm diameter graphite die lined with graphite paper and gently enclosed between two graphite punches. The powders were cold compacted using a uni-axial pressure of 30 MPa before being transferred in the die into a Dr Fritsch DSP 507 FAST machine. The consolidation chamber was evacuated to 1 mbar and maintained at this pressure during the sintering process. The cold compacted green bodies were heated from room temperature to 900 °C–1200 °C at a rate of 120 °C min\(^{-1}\) then held for 5 min at 900 °C–1200 °C, before cooling down naturally. During the first heating step, the pressure was gradually increased to 50 MPa and then maintained during the high temperature dwell time, before being progressively released during the final cooling step. The FAST current and voltage passing through the die/punch/green body arrangement was 300–900 A and 0.6–1.2 V respectively.

The 20 mm × 3–5 mm thick FAST disks were characterised by several techniques, including x-ray diffraction (XRD), scanning electron microscopy (SEM) and magnetometry. The XRD measurements were performed using a PANalytical Empyrean diffractometer with Cu\(_{K\alpha}\) radiation (\(\lambda = 0.154\) nm) at 40 kV and 40 mA. The lattice parameter, crystallite size, strain and weight fraction of the different phases present in the samples were estimated from the XRD patterns using Rietveld refinement (PANalytical HighScore Plus software). The weight fraction of the different phases was estimated by using the Hill and Howard method [14], implemented in HighScore Plus. Instrumental broadening of peaks was corrected using a Si standard analysed under the same scan conditions. The SEM analysis was performed in a Zeiss Merlin Field Emission Gun (FEG) SEM system operating at 10 kV, equipped with an Oxford Instrument 150 mm\(^2\) Xmax EDX detector. SEM samples were mounted in carbon loaded bakelite and then ground with SiC papers up to 4000 grit before being polished using colloidal silica. The bulk density of the sintered samples was measured in isopropanol using Archimedes’ method. Magnetisation measurements were acquired with a quantum design physical property measurement system vibrating sample magnetometer (VSM) on cubic samples cut from consolidated pellets, with dimensions of approximately 2 × 2 × 3 mm, and with the long axis aligned with the applied field. Connectivity measurements were performed using four-point transport measurements in a CTICryogenics closed cycle.
helium cryocooler (22C CRYODYNE) using samples 2.6–4.8 mm in width and 0.6–0.8 mm thick, with voltage taps 4 mm apart. A DC current of 0.2 A was provided by a Keysight E3631A Programmable DC Power Supply and a Keithley 2000 Digital Multimeter were used to measure the voltage. Gold coatings were first made by plasma deposition using a mask with 2 mm wide slits. The contacts were then made on these gold coated regions using electrodag.

3. Results and discussion

3.1. X-ray diffraction

Typical XRD scans of MgB₂ samples processed between 900 °C and 1200 °C are presented in figure 1, and table 1 shows the results of the XRD refinements and the density measurements. The relative bulk density of the samples was found to increase systematically with processing temperature, from 68% up to 96% for the specimens sintered at 900 °C and 1200 °C respectively. The XRD analysis shows that the impurity phase content in the bulk samples increases with increasing processing temperature. The MgO content increases slightly from 5 wt% in the as-received powder up to 8 wt% in the sample sintered at 1200 °C. The amount of MgB₄ increased more significantly, reaching 16 wt% in the sample processed at 1200 °C, more than double the concentration found in the as-received powder. The decomposition reaction 2MgB₂ → MgB₄ + MgO, that occurs above ≈900 °C [15, 16], explains the increase in MgB₄ at higher processing temperatures. In addition, the average MgB₂ crystallite size is found to increase systematically with temperature, reaching nearly 170 nm in the highest temperature sample compared to 100 nm in the as-received powder. A similar trend is observed for MgO, with the sample processed at 1200 °C having an average MgO size almost twice that in the specimen sintered at 900 °C. However, the MgO crystallite size of the powder was larger than for the bulk samples sintered at 900 °C and 1000 °C. This was probably caused by the formation of fine MgO particles during the sintering process, lowering the average crystallite size compared to the as-received powder. All the consolidated samples showed a higher MgO fraction which suggests that new MgO particles were formed during sintering. This was also observed by Matthews et al [17] in composite MgB₂ bulks manufactured by FAST.

The α-axis lattice parameter is found to decrease with increasing processing temperature, as previously observed by Aldica et al [7] in samples processed at the same temperature but for longer dwell times. They attributed this effect to a higher level of carbon substitution (coming from the graphite die) which is well known to reduce the α-axis lattice parameter of MgB₂ [18]. However, we observe a slight increase in c-axis lattice parameter with processing temperature, which is not expected for carbon doping. The inhomogeneous strain, derived using Rietveld analysis from the peak broadening, increases slightly with processing temperature. This could be because larger residual strains are induced when cooling from higher sintering temperatures. Alternatively, it may indicate that there is chemical inhomogeneity, possibly as a result of increased carbon doping of the outer edges of the samples from the graphite die during the high temperature process, leading to spatially varying lattice parameters which present as inhomogeneous strain.

3.2. Scanning electron microscopy

Figures 2 and 3 show backscattered images at different magnifications (250× and 5000× respectively) of the samples processed at (a) 900 °C, (b) 1000 °C, (c) 1100 °C and (d) 1200 °C. At low magnification (figures 2), 4 different contrast levels can be observed. These correspond to 3 solid phases, MgB₂ (light grey), MgB₄ (dark grey) and MgO (white), and to porosity (black). This phase assignation has been confirmed by EDX. The sample sintered at 900 °C shows a poorly connected microstructure containing a significant volume fraction of pores, and containing large 50–100 μm MgB₂ particles surrounded by smaller 5–50 μm MgB₂ particles. In contrast, the sample processed at 1200 °C has a very dense microstructure with hardly any porosity. The large reduction in porosity with increasing temperature observed by SEM is in good agreement with the density measurements presented in table 1.

The MgB₄ phase consists of large particles 10–50 μm in diameter, randomly distributed in the MgB₂ matrix, as shown in figure 2. Samples processed at higher temperatures contain a larger volume fraction of MgB₄, with the sample processed at 1200 °C estimated by image contrast analysis (using the software Image J) on figure 2(d) to include ≈13.4 vol% MgB₄. This corresponds to ≈13 wt% MgB₄ which is similar to the value of 16 wt% calculated from the XRD results on the same sample.

The micrograph in figure 3(a) shows the internal structure of one of the large, MgB₂ particles in the 900 °C sample at higher magnification. It is clear that even these apparently dense particles contain considerable internal porosity. The size and volume fraction of these pores are seen to be drastically reduced by increasing the sintering temperature, as
expected from the increased diffusion rates at high temperature. The sample processed at 1200 °C shows only a very small number of sub-micron pores, in contrast with the specimen sintered at 900 °C which contains a large fraction of 1–5 μm pores. The sintering temperature also has a significant effect on the size of the MgO particles. Very fine MgO particles with a diameter under 100 nm can be seen in all the specimens, but large MgO particles with a diameter up to 1 μm were only found in the sample processed at 1200 °C, which on close inspection are seen to be located at grain boundaries where diffusion is fast enough for considerable coarsening to occur. The volume fraction of MgO in the sample sintered at 1200 °C is estimated by image contrast analysis of figure 3(d) to be 5.4 vol% (≈7 wt%) which is consistent with 8 wt% estimated by XRD. Figure 3(d) also shows electron backscatter channeling contrast which reveals that the matrix of these well compacted samples is actually a fine polycrystalline MgB2 microstructure composed of grains with a diameter of a couple of microns.

Table 1. XRD characterisation and relative density of the different bulk samples made using the FAST and the as received MgB2 powder. The estimation of the precision is presented in supplementary information. Available online at stacks.iop.org/SUST/33/054003/mmedia.

| Sample | MgO (wt%) | MgB4 (wt%) | Apparent and relative density (g cm⁻³ –%) | MgB2 crystallite size (nm) | MgB2 strain (%) | MgO crystallite size (nm) | MgB2 α-axis (Å) | MgB2 c-axis (Å) |
|--------|-----------|------------|------------------------------------------|---------------------------|-----------------|--------------------------|----------------|----------------|
| Powder | 5         | 7          | —                                        | 100                       | 0.11            | 45                       | 3.086          | 3.524          |
| 900 °C | 7         | 11         | 1.81/68                                  | 120                       | 0.12            | 30                       | 3.085          | 3.525          |
| 1000 °C| 8         | 13         | 2.02/75                                  | 130                       | 0.12            | 38                       | 3.085          | 3.526          |
| 1100 °C| 8         | 16         | 2.32/86                                  | 140                       | 0.13            | 44                       | 3.084          | 3.527          |
| 1200 °C| 8         | 16         | 2.58/96                                  | 170                       | 0.14            | 54                       | 3.084          | 3.528          |

| Precision | ±0.4 | ±1.1 | — | ±12 | ±0.005 | ±4 | ±0.0002 | ±0.0003 |

3.3. Magnetisation measurements

Table 2 and figure 4 summarise the superconducting properties of the samples extracted from magnetisation-temperature (M–T) curves and magnetic hysteresis loops. Figure 4(a) shows the susceptibility of the samples sintered at 900 °C–1200 °C as a function of temperature obtained using a measurement field of 5 mT, after correcting for demagnetising effects. All the samples show a very similar onset critical temperature (Tc) around 38.7 K, but the width of the superconducting transition ΔTc decreases from 1.7 to 0.4 K as processing temperature increases. This suggests that the lower processing temperatures are not sufficient to fully recover the disorder that is present in the as-received MgB2 powder. Figures 4(b) and (c) show the effect of applied field on the width of the magnetic hysteresis loops, defined as |ΔM| = \frac{|m_i - m_0|}{V} = 2M_{irr}, where m_i and m_0 are the magnetic moments corresponding to the increasing and decreasing field branches respectively, M_{irr} is the irreversible component.
of the magnetisation and V is the sample volume. Increasing the processing temperature increases the measured $\Delta M$ values over the majority of the field range at both 4.2 and 20 K. The $J_c$ values presented in table 2 have been extracted from $\Delta M - B$ data using the standard Bean model for samples with dimensions $a$, $b$ and $c$ with the applied field $\parallel c$ and $b > a$, given in equation (1) [19]

$$J_c = \frac{2\Delta M}{a(1 - \frac{a}{b})}. \quad (1)$$

However, this model assumes that macroscopic currents can flow around a perfectly connected and homogeneous bulk sample. In porous samples the value of $J_c$ calculated will be a lower bound of the intrinsic, micro-scale $J_c$. Due to the uncertainty of the length scale of the current loops induced in our sintered specimens (discussed below), instead of presenting nominal $J_c$ values in figures 4(b) and (c), we have chosen to present the measured values of $\Delta M$.

Understanding the origin of the differences in $\Delta M$ behaviour is complicated because it depends on the intrinsic $J_c$ of the material, as well as extrinsic factors such as the effective cross-sectional area for current flow (electrical connectivity) and the length scale of the circulating current paths in the sample. The intrinsic $J_c(B,T)$ is itself influenced both by the micro/nano scale pinning landscape and how ‘dirty’ the superconducting phase is. Increasing disorder and chemical impurity substitution in the MgB$_2$ lattice makes the superconductor dirtier, and is known to lead to higher upper critical fields and reduced anisotropy [20] which will increase $J_c$ performance. In the low field region, vortices are separated by relatively large distances and so it is relatively easy to achieve strong pinning and high intrinsic $J_c$. Therefore changes in $\Delta M$ at low field are likely to be dominated by the extrinsic factors.

The volume fraction of MgB$_2$ estimated from the XRD weight fractions in table 1 are 83 vol% and 77 vol% for the samples processed at 900 °C and 1200 °C, respectively. The total superconducting fraction is then simply the product of the MgB$_2$ volume fraction and the relative density of the sample. The samples sintered at 900 °C and 1200 °C have an estimated total superconducting fraction of 56 and 73 vol% respectively, which represents an improvement of 30% by processing at higher temperature.

The effect of poor connectivity on $J_c$ values derived from magnetic measurements is explained qualitatively in figure 5. The Bean model, given in equation (1), is typically used to extract $J_c$ from the width of magnetic hysteresis loops ($\Delta M$). However, it assumes that circulating supercurrents flow macroscopically around the entire specimen. This ideal case corresponds to a fully dense, homogeneous and well connected sample as represented in figure 5(b). In this case, the macro-scale $J_c$ estimated from the Bean model is a good approximation of the intrinsic, micro-scale $J_c$.

Figure 5(a) shows a schematic microstructure of a poorly sintered material in which supercurrents are only able to circulate within the particles (each of which may contain many micron-sized grains) owing to the poor particle connectivity. In that case, the total moment generated by these micro-scale supercurrents is much smaller and the intrinsic $J_c$ values inside the particles. The two extreme cases depicted in figure 5 are similar to the microstructures of the samples processed at 900 °C and 1200 °C shown in figures 2(a)
and (d). To explore whether the reduction in ΔM in the low density samples can be explained simply by extrinsic effects, $J_c(B)$ values at 20 K for the sample processed at 900°C, $J_{c,macro}$ and $J_{c,micro}$ values have been computed using two versions of the Bean model representing extremes of connectivity. In the macro-scale model, the sample was considered as a perfectly connected, homogeneous cuboid and sample dimensions were used in equation (1) to compute $J_{c,macro}$. In contrast, the micro-scale model considers that the sample is made of individual (spherical) particles that are electrically isolated from one another (i.e. supercurrents cannot flow between adjacent particles). In this case, the particle median size, $d_{0.5}$, (measured on the initial powder using a laser diffractometer) was used in Bean’s model, instead of the dimensions of the whole sample, to calculate $J_{c,micro}$ using equation (2)

$$J_c = \frac{32 \Delta M}{3\pi d_{0.5}}$$ (2)

These two models give estimated lower and upper bounds of the intrinsic $J_c$ of the material, as shown in figure 4(d). Comparing $J_{c,micro}$ of the porous 900°C sample with $J_{c,macro}$ of the dense, well connected bulk suggests that lower processing temperatures actually lead to higher intrinsic $J_c$ performance. This is consistent with the microstructural observations that lower processing temperatures lead to finer microstructures and the dirtier superconducting phase, both of which should result in higher intrinsic $J_c$ values.

3.4. Connectivity measurements

To estimate the effective cross-sectional area for macroscopic current transport in our bulk samples, four-point transport measurements have been performed to obtain the normal state electrical resistivity as a function of temperature. Following the analysis of Collings et al [13], we have fitted the Bloch-Gruneisen function (3) to our data, enabling us to extract the residual resistivity, $\rho_0$, the Debye temperature, $\theta_D$, and the scale factor, $F$, which is related to the percentage connectivity by $K = \frac{\rho_0}{\rho}$ [21]. To obtain the materials constant, $K$, we initially fitted equation (3) to reference single crystal data

### Table 2. Superconducting properties of the MgB2 specimens processed at 900°C, 1000°C, 1100°C and 1200°C. $J_c$ values were estimated using the macro model.

| Sample | $T_c$ (K) | $\Delta T_c$ (K) | $J_c(5T)$ at 4.2 K (A m$^{-2}$) | $J_c(0T)$ at 20 K (A m$^{-2}$) | $J_c(3T)$ at 20 K (A m$^{-2}$) |
|--------|-----------|-----------------|-------------------------------|-------------------------------|-------------------------------|
| 1200 °C | 38.7 | 0.4 | $4.6 \times 10^7$ | $3.3 \times 10^9$ | $3.8 \times 10^7$ |
| 1100 °C | 38.7 | 0.4 | $4.6 \times 10^7$ | $3 \times 10^9$ | $3.8 \times 10^7$ |
| 1000 °C | 38.6 | 0.6 | $2.6 \times 10^7$ | $1.8 \times 10^9$ | $2.2 \times 10^7$ |
| 900 °C | 38.6 | 1.7 | $1.2 \times 10^7$ | $0.55 \times 10^9$ | $0.87 \times 10^7$ |

Figure 4. Superconducting properties of the MgB2 samples processed at 900°C, 1000°C, 1100°C and 1200°C. (a) susceptibility, (b) ΔM–B curve at 4.2 K, (c) ΔM–B curve at 20 K, (d) $J_c$–B curve at 20 K.
Figure 6 clearly shows that the connectivity from Eltsev et al. following the analysis outlined by Collings et al [13].

\[
\rho(T) = F \left[ \rho_0 + \left( \frac{k}{\theta_D} \right)^5 \int_0^{\theta_D} \frac{e^z - 1}{1 - e^z} dz \right]
\]

Figure 6 clearly shows that the connectivity (effective cross-sectional area for macroscopic current transport) in the 900 °C sample is very low, improving by a factor of ≈6 on increasing the processing temperature to 1200 °C. This confirms that it is appropriate to use the micro-model for estimating \( J_c \) from magnetisation data for the 900 °C sample. The 1200 °C sample also has a reduced cross-sectional area for current transport, so the macro-model is also likely to underestimate the true intrinsic \( J_c \) in this sample. The residual resistivity value is seen to decrease systematically with increasing processing temperature, suggesting the MgB\(_2\) lattice contains fewer defects and/or less impurity in solid solution. This is likely to result in the superconductor becoming ‘cleaner’ according to the definition of Anderson [23].

3.5. Pinning force analysis

To explore whether the dominant pinning mechanisms are affected by processing temperature, normalised pinning force density curves at 4.2 and 20 K are shown in figures 7(a) and (b). The reduced field \( b = \frac{B}{B_{irr}} \) has been calculated using irreversibility field \( (B_{irr}) \) values estimated using the same method as Martinez et al by linear extrapolation of Kramer plots \( (B^2J_f^2) \) in the high field range, ignoring the tail which is attributed to flux creep [24]. As the Kramer plots are not linear, particularly for the high temperature processed samples, we estimate that the uncertainty in \( B_{irr} \) values is as high as ±0.5 T. In addition, our magnetisation measurements were carried out in VSM mode and the field inhomogeneity the sample is exposed to as it vibrates is expected to lead to underestimation of the true irreversibility field [25].

Table 3 shows the \( B_{irr} \) values used in our analysis, together with peak positions and \( p, q \) values obtained from fitting the data to the general function \( f_p \propto b^p(1-b)^q \). Pinning in MgB\(_2\) is generally considered to be dominated by two-dimensional grain boundary pinning [26, 27]. However, our well-connected bulk samples processed at temperatures of 1000 °C and above have curves that deviate considerably from the \( f_p = b^{p}(1-b)^{q} \) function predicted by the core-pinning model of Dew-Hughes for surface normal pinning [28] and Kramer’s flux line lattice (FLL) shear model [29]. In particular, the 1100 °C sample has a peak position at around \( b_{peak} = 0.3 \) rather than the \( b_{peak} = 0.2 \) predicted for grain boundary pinning, and the 1000 °C processed sample shows two peaks in the pinning force curve, the main one at \( b_{peak} \approx 0.2 \) with a secondary peak \( b_{peak} \approx 0.35 \). This may indicate that there is a significant contribution from ‘point normal pinning’, which Dew-Hughes has described by the function \( f_p = b(1-b)^2 \), and having a peak at \( b_{peak} = 0.33 \) [28]. This could arise from the presence of non-superconducting secondary phase particles (e.g. MgO and MgB\(_4\)) with all dimensions smaller than the flux line spacing. However, it is well known that the Labusch form of the shear modulus of the flux line lattice used in the classical FLL shear model, \( C_{66} \propto (1-b)^2 \) [30], is only...
accurate at high field [31]. Brandt derived a different form of the shear modulus from Gorkov’s microscopic theory that is valid over almost the entire field range [32]

\[ C_{66} = b(1 - b)[1 - 0.58b + 0.29b^2]. \]  

(4)

Modifying the classical Kramer model with the Brandt form of the \( C_{66} \) parameter leads to a shift in the peak position to the higher field of \( b_{\text{peak}} \approx 0.4 \), as shown in figure 7(c). Therefore, it is possible that the shifted peak position observed in our 1100 °C and 1200 °C processed samples is still consistent with a grain boundary pinning mechanism. It is worth noting that whilst it is clear that the form of \( C_{66} \) used by Kramer is not correct over the entire field range [31], extensive studies on Nb3Sn show that the \( f_p \propto b^p(1 - b)^q \) form is a good fit to the experimental data [33]. It is not fully understood why this is the case. In general, in our data there is a systematic decrease in \( p \) value of the fit to \( f_p \propto b^p(1 - b)^q \) with decreasing processing temperature, changing from \( p > 1 \) for the highly connected samples to \( p < 1 \) in the porous samples, as shown in table 3. These correspond to very different \( J_c(b) \) behaviour at low field: for \( p < 1 \), \( J_c \) rapidly increases as \( b \to 0 \), whereas for \( p > 1 \), \( J_c \) levels off and starts to decrease as \( b \to 0 \). However, care must be taken when interpreting \( p \) values because at very low fields, where the flux line spacing is large, the continuum assumptions of the FLL shear model breaks down and other defects which are present in low densities may start to contribute to pinning [24].

In addition, it can be seen in figures 7(a) and (b) that there is a large deviation in the peak shape on the high-field side of the peak for the well-connected high temperature
processed samples, with pinning force density decreasing more rapidly with field than predicted by either the grain boundary or point pinning models. This concave shape corresponds to significantly higher $q$ values than the $q = 2$ predicted by the grain boundary pinning or point pinning models, and has been observed previously by other groups [13, 24]. Wordenweber et al attributed the high $q$ values observed in c-axis aligned YBCO to inhomogeneity in the superconducting properties [34]. However, Eisterer et al point out that anisotropy needs to be taken into account to explain the shape of $J_c(B)$ curves in polycrystalline MgB$_2$ [20]. Superconductivity in grains aligned in unfavourable directions relative to the applied field will effectively switch off at high fields, reducing the effective cross sectional area for supercurrent. Defining $s$ as the fraction of grains that are superconducting, the effective cross sectional area, $A_s$, is given by $A_s = A_0s_0$ where $s_0$ is the geometric cross sectional area. The term $A_s$ can be modelled with a power law using percolation theory, where $s_s$ is the percolation threshold and $\alpha$ depends on the geometry of the system and $n$-value of the current–voltage power law

$$A_s(s, s_s) = \left(\frac{s - s_s}{1 - s_s}\right)^\alpha.$$  

(5)

When the fraction of superconducting grains decreases to the threshold value, $s_s$, there is no longer a macroscopic superconducting path through the sample, and $J_c$ will drop to zero. Following the analysis of Eisterer et al [20], we will take the fraction of grains that are superconducting at a given field to be the average of the maximum fraction, $s_{\text{max}}$ and the percolation threshold, $s_{s_s}$, with $s_{\text{max}}$, given by the angular dependence of the upper critical field

$$s_{\text{max}}(B) = \left[\left(1 - \frac{B_{c2}^{ab}B}{B_{c2}^2}\right) - 1\right]^{\gamma},$$  

(6)

where $B_{c2}^{ab}$ is the critical field with applied field parallel to ab and $\gamma = \frac{R_e^2}{R_{irr}^2}$ is the anisotropy. This assumes that the volume fraction of MgB$_2$ is 1. Combining equations (5) and (6) gives an expression for $A_s(\delta, s_s)$ which has meaningful values greater than 1 in the low field region below a threshold field, $B_{th}$. Therefore here we assume the relative cross sectional area for supercurrent is $A_s = 1$ for $b < b_h$ and $A_s(b) = A_s(\delta, s_s)$ for $b > b_h$. This is not strictly physical because for some of this range $s_{\text{max}} > 1$, but it is a reasonable approach for investigating the general effect of anisotropy on the shape of pinning force curves.

Combining $A_s(b)$ with the classical Kramer model, the pinning force density as a function of field is given by $f_p(b) \propto b^\beta(1 - b)^\gamma A_s(b)$. Figure 7(d) shows how the high field region of the pinning force curve shape is adjusted by incorporating this effect of anisotropy, using reasonable values of $s_s = 0.25$ and $\alpha = 1.79$, after Eisterer et al [20]. Whilst the exact shape of the curve is sensitive to the values of $\frac{R_e}{R_{irr}}$ and $\gamma$, it is clear that incorporating anisotropy into the model can reproduce the rapid $f_p$ decrease with $b$ on the high-field side of the peak. Fitting the general $f_p \propto b^\beta(1 - b)^\gamma$ to curves simulated using this model, we find that $q$ values increase with increasing $\frac{R_e}{R_{irr}^2}$ and increasing anisotropy, $\gamma$. At 20 K, using $B_{c2} \approx 10$ T and $\gamma \approx 4$ gives a $q$ value of $\approx 4$, which is consistent with the experimental value for the well-connected sample processed at 1100 °C. Figure 8 compares the various models with the experimental data for the 1100 °C sample at 20 K and shows that the shape of the curve can be reasonably well reproduced using the Eisterer percolation model to account for anisotropy [20], taking $B_{c2}^{ab} \approx 10$ T, $B_{irr} \approx 4$ T and $\gamma \approx 4$.

However, the sample processed at the low temperature of 900 °C has a broader peak shape and is reasonably well fitted by the classical grain boundary pinning model (at 4.2 K) and the point pinning model (at 20 K) without taking anisotropy into account. Since the MgB$_2$ samples processed at low temperature are likely to be dirtier as discussed above, we would expect them to have increased $B_{c2}$ and decreased $\gamma$ values, both of which will reduce the effect of anisotropy (see figure 8). In addition, there may be other effects owing to the current paths being on the length scale of the particles in this poorly connected sample rather than on the length scale of the entire bulk sample as expected in samples processed at higher temperature.

4. Conclusions

MgB$_2$ pellets were manufactured at temperatures ranging from 900 °C to 1200 °C using the field assisted sintering technique. The sintering temperature had a large influence on the microstructure of the sintered specimens, with samples densifying and microstructures coarsening as the temperature increased as expected from the higher diffusion rates. Relative bulk densities as high as 96% have been achieved by sintering for short times at 1200 °C. The MgO and MgB$_4$ content also increased with the processing temperature. All the specimens had similar $T_C$ and $B_{irr}$ values but very different $\Delta M(B)$ curves. In particular, the sample processed at 1200 °C had the highest $\Delta M$ over the entire field range and showed a 6 fold increase in $\Delta M(0$ T) at 20 K compared to the specimen sintered at 900 °C. This large improvement in $\Delta M$ was mainly attributed to the increase in connectivity. The significant difference between the $J_c$ values computed with the macro and macro versions of the Bean model demonstrates the difficulty in estimating the true intrinsic $J_c$ of real bulk samples which typically have a mixed behaviour, i.e. neither perfect or zero connectivity, and highlights the importance of rigorous microstructural analysis. Pinning force analysis showed the limitations of using the classic Kramer flux lattice shear model to describe the behaviour of our MgB$_2$ specimens. Improved fits could be obtained to the high field side of the peak by considering anisotropy effects that essentially decrease the effective cross-sectional area for current flow with increasing applied field. The peak shift to higher reduced field values observed in the high temperature processed samples is usually attributed to a point pinning contribution in addition to grain boundary pinning. This may be a result of the increase in grain
size with processing temperature reducing the contribution to the volume pinning force from grain boundary pinning. However, we found that this peak shift could also be reproduced using a more accurate model for the flux lattice shear modulus combined with Kramer’s model, making it difficult to come to a definite conclusion about whether pinning mechanisms are influenced by the processing temperature.

In conclusion, processing at the high temperature of 1200 °C improves densification and hence connectivity of bulk MgB2. However the intrinsic $J_c$ of the material is higher in samples processed at the lower temperature of 900 °C, owing to slower diffusion rates leading to finer scale microstructures and preventing annealing out of disorder that increases the upper critical field. This suggests there is considerable scope for further improvements to be made in the performance of ex situ MgB2 bulk materials by a detailed understanding of the complex interaction between microstructure and superconducting properties.

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