Design and characterisation of \textit{ex situ} bulk MgB$_2$ superconductors containing a nanoscale dispersion of artificial pinning centres

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Abstract

MgB$_2$ pellets containing a nanoscale dispersion of artificial pinning centres have been successfully manufactured through a powder metallurgy route based on the oxide dispersion strengthened (ODS) concept more usually used for steels and superalloys. Commercial MgB$_2$ powder and Y$_2$O$_3$ nanopowder were mechanically alloyed in a high energy planetary ball mill and consolidated using the field assisted sintering technique. The composite powders were ball milled for different times up to 12 h and characterised by means of particle size analysis, x-ray diffraction (XRD) and scanning transmission electron microscopy (STEM). The microstructure and superconducting properties were characterised by density, XRD, STEM and magnetic property measurements. The powder microstructure comprised Y$_2$O$_3$ particles dissolved into the MgB$_2$ matrix. After consolidation there was a near-uniform dispersion of precipitated YB$_4$ and MgO particles. A bulk 0.5 wt% Y$_2$O$_3$-MgB$_2$ composite showed the best superconducting performance with a significant improvement in $J_c$ at high field compared with unmodified MgB$_2$, and only a small reduction in $T_c$. The results suggest that the ODS concept is promising to improve the superconducting properties of MgB$_2$.

Keywords: MgB$_2$, bulk, microstructure, processing

Some figures may appear in colour only in the online journal

1. Introduction

Since the discovery of its superconducting properties in 2001 [1] MgB$_2$ has become a popular and promising material for superconductivity applications due to its interesting combination of properties. The critical temperature ($T_c$) of 39 K is the highest of any binary compound at ambient pressure, and makes it more suitable for helium-free applications than other low temperature superconductors such as NbTi and Nb$_3$Sn. In comparison to most high temperature superconducting compounds (HTS), MgB$_2$ does not contain any rare earth or toxic elements and is much easier to process [2]. Unlike HTS materials, MgB$_2$ bulks do not need to be processed in single grain (or low misorientation polycrystal) form because the larger coherence length in MgB$_2$ means that high angle grain boundaries do not act as weak links.

To improve the superconducting properties of MgB$_2$, carbon doping or the addition of oxide particles to increase the critical current density ($J_c$) has been used. Carbon doping has led to significant improvements in $J_c$ at high field but also causes a severe reduction in $T_c$ [3, 4]. Simple oxide additions in both \textit{in situ} and \textit{ex situ} processed materials can improve $J_c$ values at high field, but decrease $J_c$ at low field without having a significant effect on $T_c$ [5–9]. Others have reported a decrease in $J_c$ at both high and low fields [10, 11]. The effect of different additions on the superconducting properties of MgB$_2$ are summarised in table 1.

Most of these studies suggest that $J_c$ improvements at high field is due to the presence of nanoscale pinning centres, although most reports do not show any direct evidence of pinning centres and their characteristics; the decrease in $J_c$ at low field is also usually unexplained.
This study investigates a new route to manufacture bulk MgB$_2$ pellets of up to 20 mm diameter, containing a nanoscale dispersion of artificial pinning centres based on the oxide dispersion strengthened (ODS) concept more usually used in steels and superalloys. The aim is to first dissolve Y$_2$O$_3$ into the MgB$_2$ lattice by severe plastic work introduced by mechanical alloying, and second to re-precipitate Y-based nano particles during consolidation using the field assisted sintering technique (FAST), also known as resistive sintering [12] or spark plasma sintering [13]. The microstructure and superconducting properties of the bulks have been carefully characterised to provide a better understanding of the effect of the different microstructural features on $I_c$ and $T_c$ values.

### 2. Experimental details

Mixtures of pre-synthesised MgB$_2$ (purity: 99%, Alfa Aesar) and nano Y$_2$O$_3$ (20–40 nm, purity: 99.999%, PI KEM Ltd) powders were sealed into stainless steel jars with stainless steel balls under an Ar atmosphere. The total mass of the powder was 10 g with a ball-to-powder ratio of 10:1. Mechanical alloying was conducted in a Fritsch P5 planetary ball mill rotated at 350 rpm in repeating cycles of 10 min of milling followed by a 20 min pause to prevent the powders from overheating. After different milling times (20 min, 1, 3, 6 and 12 h) the powders were recovered in a glove box under Ar.

For consolidation, the composite powders were poured into a 20 mm diameter graphite die lined with graphite paper and gently enclosed between two graphite punches. The powders were then cold compacted using a uni-axial pressure of 30 MPa before being transferred in the die into a Dr Fritsch DSP 507 FAST apparatus. 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 1150 °C at a rate of 120 °C min$^{-1}$ then held for 5 min at 1150 °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 at 1150 °C, 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 powders and FAST disks (20 mm in diameter and 4 mm in thickness) were characterised by several techniques, including x-ray diffraction (XRD), scanning transmission electron microscopy (STEM), powder particle analysis, density measurements and magnetometry. The XRD measurements were performed using a PANalytical Empyrean diffractometer with CuK$_x$ radiation (λ = 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 spectra 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 STEM analysis was performed in a JEOL 3000F at an accelerating voltage of 300 kV, equipped with a high angle annular dark field (HAADF) detector and an Oxford Instrument EDX detector. STEM specimens were prepared by cutting 3 mm disks from thin slices made from the consolidated pellets. The disks were then mechanically polished to approximately 100 μm before being dimpled and finally thinned to perforation with a Fischione 1010 Ion Mill. The transmission Kikuchi diffraction (TKD) investigations were carried out in a Zeiss Merlin field emission gun (FEG) SEM system operating at 20 kV, equipped with a Bruker e-flash high-resolution electron back scattered diffraction (EBSD) detector and an OPTIMUS TKD head. Particle size analysis was performed using a Malvern Master-Sizer laser diffractometer by dispersing the powder in deionised water. The bulk density of the sintered samples was measured in isopropanol using the Archimede method. Magnetisation measurements were acquired with a quantum design physical property measurement system (PPMS) vibrating sample magnetometer (VSM) on cubic samples cut from consolidated pellets, with dimensions of approximately 2 × 2 × 3 mm. The critical current density was calculated from the full magnetic hysteresis loops using Bean’s model [15].
3. Results and discussion

3.1. MgB\textsubscript{2} based powders

The median particle diameter of the 0.5 wt\% Y\textsubscript{2}O\textsubscript{3}-MgB\textsubscript{2} composite powder as a function of milling time and their corresponding XRD spectra are shown in figure 1. There was an initial sharp reduction in particle diameter from approximately 40 μm for the pristine powder to 4 μm after only 10 min of milling. The particle diameter then stabilised at 1.5 μm after 1 h of milling, and this is usually interpreted as the point where the rate of fragmentation equals the rate of agglomeration. MgB\textsubscript{2} is intrinsically relatively brittle, leading to the rapid diameter reduction.

The XRD spectra revealed three phases: MgB\textsubscript{2}, MgB\textsubscript{4} and MgO. The small fraction of Y\textsubscript{2}O\textsubscript{3} added (0.5 wt\%) was below the XRD detection limit, hence no Y\textsubscript{2}O\textsubscript{3} peaks were observed. MgB\textsubscript{4} and MgO are impurities commonly found in MgB\textsubscript{2} and often present in commercial powders \[16, 17\]. After milling, the characteristic peaks of all three phases in figure 1 decreased progressively in intensity and became broader, resulting in both an increase in inhomogeneous strain and/or a reduction in effective crystallite size, as shown in table 2. Table 2 summarises the results of Rietveld refinement of the XRD spectra. The pristine powder contained approximately 5 wt\% MgO and 7 wt\% MgB\textsubscript{4}, and the fraction of these impurities increased with milling time. In particular, the MgO fraction increased up to 10.9 wt\% after 12 h. Therefore, despite using an Ar filled glove box, it was not possible to fully exclude residual oxygen that reacted with the freshly formed surface of the MgB\textsubscript{2} particles during ball milling. The small increase in MgB\textsubscript{4} fraction was probably a refinement artifact rather than a change in composition. The MgB\textsubscript{4} peaks were relatively weak and difficult to fit during the Rietveld refinement, and the signal to noise ratio decreased with ball milling time which may have led to an overestimation of the total intensity of the MgB\textsubscript{4} peaks relative to the total diffracted intensity.

As commonly seen in mechanically alloyed powders, the crystallite size of MgB\textsubscript{2} decreased and the strain increased with milling time (table 2). Although the refinement of the particle diameter stopped after 1 h of milling, the XRD spectra suggested that refinement of the microstructure (crystallite size) continued. While qualitatively this behaviour is similar to that widely reported for ODS steels, it is perhaps surprising that a brittle compound shows essentially identical trends. Further, there was a gradual increase in the \textit{a} and \textit{c}-axis of the MgB\textsubscript{2} lattice with increasing milling time. Yttrium has a larger atomic size (2.32 Å) than either magnesium or boron (1.73 and 1.92 Å respectively), and the increase in lattice volume may be due to the dissolution (and possible dissociation) of Y\textsubscript{2}O\textsubscript{3} into the MgB\textsubscript{2} lattice. Again, similar phenomena are seen in metallic ODS solid solutions at long milling times \[18, 19\].

The composite powders were further characterized by STEM analysis. High angle annular dark field (HAADF) images of individual powder particles were acquired along with the corresponding Y and O EDX maps. Analysis was conducted on several particles for each milling condition and representative images and EDX maps of powder ball milled for 10 min, 1 and 12 h are shown in figure 2.
After 10 min of milling, undissolved Y$_2$O$_3$ particles of approximately 20–50 nm diameter were embedded in the MgB$_2$ matrix. The corresponding Y and O maps indicated that Y and O concentrations were co-located. After 1 h of milling, the image contrast was more difficult to interpret due to the high concentration of defects (vacancies and dislocations) introduced by mechanical alloying, and few discrete Y$_2$O$_3$ particles could be resolved. Again, in the EDX maps there were areas comparatively richer in both Y and O, but both elements were now more widely dispersed. This trend was confirmed after 12 h of milling where no Y$_2$O$_3$ particles could be resolved and the EDX maps showed a much more homogeneous distribution of both Y and O. Consistent with the XRD results above, this suggests that the Y$_2$O$_3$ nanoparticles have dissolved into the MgB$_2$ lattice. In order to further investigate the evolution of the Y$_2$O$_3$ phase during the mechanical alloying process, composite powders containing a much higher fraction of Y$_2$O$_3$, so that it might be more easily resolved, were fabricated. Figure 3 shows XRD spectra from MgB$_2$ + 10 wt% Y$_2$O$_3$ as a function of milling time.

The initial mix of powders showed a strong (222) Y$_2$O$_3$ reflection, which was still visible after 10 min of milling. However, this peak decreased in intensity after 1 h, and vanished at longer ball milling times. Thus it was concluded that for the composite powders, even when relatively large fractions of Y$_2$O$_3$ were added, all the Y$_2$O$_3$ was dissolved.
Table 3. Composition and processing conditions for MgB2 based pellets consolidated using the FAST.

| Sample     | Y2O3 (wt%) | Milling time (h) | Temperature (°C) | Dwell time (min) | Pressure (MPa) | Heating rate (°C min⁻¹) |
|------------|------------|------------------|------------------|------------------|----------------|------------------------|
| MgB2       | 0          | 0                | 1150             | 5                | 50             | 120                    |
| 0.5Ym1h    | 0.5        | 1                | 1150             | 5                | 50             | 120                    |
| 0.5Ym12h   | 0.5        | 12               | 1150             | 5                | 50             | 120                    |
| 2Ym12h     | 2          | 12               | 1150             | 5                | 50             | 120                    |

Table 4. Density and estimated phase fractions by Rietveld analysis for bulk MgB2-based pellets consolidated by FAST.

| Sample     | MgO (wt%) | MgB4 (wt%) | Relative density (%) | MgB2 crystallite size (nm) | MgB2 strain (%) | MgB2 a-axis (Å) | MgB2 c-axis (Å) |
|------------|-----------|------------|----------------------|---------------------------|-----------------|-----------------|-----------------|
| MgB2       | 8         | 13         | 93                   | 151                       | 0.14            | 3.0838          | 3.5279          |
| 0.5Ym1h    | 12.5      | 20.8       | 90                   | 113                       | 0.16            | 3.0836          | 3.5278          |
| 0.5Ym12h   | 15.2      | 17.3       | 87                   | 87                        | 0.2             | 3.0846          | 3.5287          |
| 2Ym12h     | 14.9      | 18.7       | 86                   | 75                        | 0.21            | 3.0844          | 3.5281          |

(Ypresumably as dissociated Y and O) from the EDS maps) into the MgB2 lattice during mechanical alloying. A further possibility, suggested for some cases of ODS steels, but for which there was no compelling evidence in this particular study, is that the Y2O3 becomes first very finely divided and then effectively amorphous (glassy) due to the excessive cold work and ultra-high defect density induced by cold milling [20, 21].

3.2. Bulk MgB2

The FAST has been successfully used by several research groups to produce dense MgB2 bulk samples [17, 22, 23]. Dancer et al [17] reported that MgB2 with a relative density of 97% could be obtained by using a temperature of 1250°C and a pressure above 50 MPa. Aldica et al [23] achieved densities ranging from 95% to 97% using a temperature of 1150°C, a pressure of 95 MPa and dwell times between 1 and 20 min. The processing conditions used in this study were chosen based on these findings.

MgB2-based pellets were manufactured from different Y2O3-MgB2 composite powders and processing conditions summarised in table 3. The three sample codes 0.5Ym1h, 0.5Ym12h and 2Ym12h correspond to bulk pellets manufactured from MgB2 + 0.5 or 2 wt% Y2O3 powders ball milled for 1 or 12 h.

The pellets were first characterized by density measurements and XRD. The bulk density, which includes both open and closed porosity, was measured using the Archimedes method, and the relative density calculated using the estimated phase fractions from the Rietveld refinement. As shown in table 4, longer milling times gave higher MgO fractions. Compared with the powders before consolidation, all consolidated pellets also showed a significant increase in MgB4 fraction after sintering at 1150°C. The decomposition reaction 2MgB2 → MgB4 + MgO occurs above 900°C–1000°C [24, 25]. The unmodified MgB2 pellet had the highest relative density of 93% while MgB2 + Y2O3 milled for 1 h had a slightly lower density of 90%, and MgB2 + Y2O3 milled for 12 h had a density below 90%. This suggests that the addition of Y2O3 and the increase in MgO fraction due to ball milling had a detrimental effect on densification, perhaps due to the higher intrinsic sintering temperature of MgO [26].

MgB2 based pellets showed a small increase in MgB2 crystallite size compared with their respective powders due to coarsening at 1150°C. Nonetheless, the relatively small crystallite size in the powder milled for 12 h was retained in the bulk samples, and finer than that of unmodified MgB2. The relatively high temperature consolidation—even for a short time of 5 min—significantly reduced the MgB2 lattice strain, typically from 0.5% down to 0.2% after sintering.

The consolidated material was again studied by STEM, and typical HAADF images along with Y and O EDX maps of the 0.5Ym1h, 0.5Ym12h and 2Ym12h samples are shown in figure 4. For all the conditions we found relatively fine MgB2 grains, typically of a diameter of a few hundred nanometres, and numerous MgO and YB4 nano-particles. As shown in figures 4(c) and (d), fine 20–30 nm MgO particles were within MgB2 grains, as well as coarser MgO up to 150 nm located at grain boundaries. Figures 4(c) and (d) show that the YB4 precipitates have a diameter ranging from 20 to 60 nm, and were mainly located at the surface of the larger MgO particles and also within MgB2 grains. No trace of discrete Y2O3 particles was detected. The presence of YB4 was confirmed by XRD and TKD, as shown in the example given in figure 5 for MgB2 + 2 wt% Y2O3. Song et al [5] also found that YB4 was formed in Y2O3 doped MgB2. In fact, YB4 can also be synthesised through the borothermal reduction of Y2O3 at temperatures around 2000°C [27]. Although the sintering temperature (here of 1150°C) was lower, local temperatures in the FAST are known to sometimes be very much higher than the ‘bulk’ reading from a pyrometer or thermocouple, even if only for a few seconds. In addition, as previously suggested, Y may be dissolved in MgB2 by milling and may react directly with MgB2 on re-precipitation to form YB4. At the same time, dissolved oxygen precipitates as MgO.
In a similar study, Mikheenko et al [6] also found that fine DyB₄ particles precipitated during resistive sintering of Dy₂O₃ doped MgB₂. MgB₂ + 0.5 wt% Y₂O₃ after 1 h of milling had a noticeably inhomogeneous YB₄ particle distribution, which mainly formed large agglomerates at grain boundaries, as shown in figures 4(a) and (b). As expected, there was a higher YB₄ fraction in MgB₂ + 2 wt% Y₂O₃ (shown in figures 4(e) and (f)), with most precipitates located at grain boundaries. For MgB₂ + 0.5 wt% Y₂O₃ milled for 12 h the size distributions of the MgO and YB₄ particles are shown in figure 6. The YB₄ particles had a monomodal distribution with most diameters between 20 and 30 nm, and an average diameter of 28 ± 10 nm. XRD spectra of MgB₂ + 10 wt% Y₂O₃ processed under the same conditions gave YB₄ fractions high enough to be detected, and Rietveld analysis gave

Figure 4. Typical HAADF images and Y (green) and O (blue) EDX maps of specimens (a), (b) 0.5Ym1h, (c), (d) 0.5Ym12h and (e), (f) 2Ym12h.
an average diameter of 35 nm, in good agreement with the STEM results. MgO showed a bimodal distribution composed of fine 20–50 nm and coarser 80–120 nm diameters, with an average diameter of 60 ± 30 nm, again similar to the 50 nm extracted from the XRD measurements.

Overall, most of the YB₄ particles nucleated on larger MgO particles, which suggested that MgO was present before YB₄ precipitation, i.e. before sintering. These large MgO particles were probably pre-existing in the as-supplied MgB₂ powder. The finer MgO particles were mainly located inside the MgB₂ grains with a diameter similar to the YB₄ precipitates, which may indicate they were formed and coarsened during the FAST process. This suggests that the addition and dissolution of Y₂O₃ in the MgB₂ matrix during mechanical alloying had the double effect of producing a fine dispersion of both YB₄ and MgO during sintering. This is dissimilar to ODS alloys where predominantly Y₂O₃ is re-precipitated, albeit with more complex transition phases sometimes involved, such as Y–Ti–O phases in Fe–Cr–Ti containing matrices [19].

The superconducting properties of the pellets are shown in figure 7 and summarised in table 5. Figure 7(a) shows the normalised susceptibility curves, with Tc values for unmodified MgB₂, MgB₂ + 0.5 wt% Y₂O₃ milled for 1 h, MgB₂ + 0.5 wt% Y₂O₃ milled for 12 h and MgB₂ + 2 wt% Y₂O₃ milled for 12 h estimated as 38.7, 38.1, 37.7 and 37.2 K respectively. Tc in MgB₂ is well-known to be affected by any deviation from an ideal MgB₂ crystal structure, and is thus sensitive to doping, strain and defect concentrations, and this explains the degradation in Tc in our samples. MgB₂ + 0.5 wt% Y₂O₃ milled for only 1 h showed the smallest Tc reduction, whereas MgB₂ + 2 wt% Y₂O₃ milled for 12 h had the lowest Tc due to the higher strain. Nonetheless, all the pellets had only a small reduction in Tc, indicating that Y₂O₃ does not have as severe an effect on Tc as carbon [4].

At 4.2 K, the high field properties are best represented on a log-scale Jc–B plot, as shown in figure 7(b). Measurements at lower fields were often compromised by excessive flux jumps below 3 T, so this is not shown in the figure. MgB₂ + 0.5 wt% Y₂O₃ milled for 1 h showed no improvement compared with unmodified MgB₂, but by contrast MgB₂ + 0.5 and 2 wt% Y₂O₃ after 12 h milling both showed an appreciable improvement in Jc over the entire field range, with MgB₂ + 0.5 wt% Y₂O₃ (12 h) displaying the best performance. This strong difference in performance can be directly related to the STEM observations. MgB₂ + 0.5 wt% Y₂O₃ (1 h) showed a relatively poor distribution of YB₄ particles, which formed agglomerates that were much larger than the coherence length of MgB₂ (ξ = 5–10 nm [2]). In consequence, these agglomerates could not act as efficient pinning centres to improve Jc. On the contrary, STEM analysis showed that MgB₂ + 0.5 or 2 wt% Y₂O₃ (12 h) had a much more homogeneous dispersion of finer YB₄ precipitates. Figures 4(e) and (f) also showed that for MgB₂ + 2 wt% Y₂O₃ (12 h) many particles were located at grain boundaries which could be detrimental to the grain connectivity and hinder macroscopic supercurrents. The improvement in Jc was probably a trade-off between an increase in pinning centre density and a degradation of grain connectivity. At 4.2 K, MgB₂ + 0.5 wt% Y₂O₃ (12 h) showed a three fold increase in Jc at 5 T and Bn was improved by 1 T compared to unmodified MgB₂.

At 20 K, unmodified MgB₂ showed the highest self-field Jc (Jc0) followed by MgB₂ + 0.5 wt% Y₂O₃ (12 h), MgB₂ + 0.5 wt% Y₂O₃ (1 h), while MgB₂ + 2 wt% Y₂O₃ (12 h) had the lowest Jc0. Many parameters can influence Jc0, including the total superconducting fraction and grain connectivity. All the MgB₂ + Y₂O₃ materials had a lower relative density and an impurity content significantly higher than unmodified MgB₂. The combination of these features controls the total superconducting fraction and explains why the unmodified MgB₂ pellet, which had the highest total superconducting fraction, also showed the highest Jc0. Due to their similar density and composition, all the Y₂O₃-containing variants had a similar total superconducting fraction so that differences in Jc0 may be due to differences in connectivity. For example, the STEM images in figures 4(a)–(f) suggested that MgB₂ + 0.5 wt% Y₂O₃ (12 h) had a better connectivity than both MgB₂ + 0.5 wt% Y₂O₃ (1 h) and MgB₂ + 2 wt% Y₂O₃ (12 h).

Figure 7(c) also shows that at 20 K, Jc at high field followed a similar trend to Jc(4.2 K; MgB₂ + 0.5 wt% Y₂O₃ (12 h) had the best Jc of 8.6 × 10⁷ A m⁻² with a two fold increase at 3 T and a 0.3 T improvement in Bn compared with unmodified MgB₂.

These results are in good agreement with the studies of Song [5] and Mikheenko [6] who observed similar Jc improvements in Y₂O₃ and Dy₂O₃ doped MgB₂. The authors found that nano-scale YB₄ or DyB₄ particles were formed.

**Figure 5.** Typical TKD phase map from MgB₂ + 2 wt% Y₂O₃ showing MgB₂ (grey), YB₄ (green) and MgO (blue).
during sintering and acted as efficient pinning centres that enhanced $J_c$, in particular at high field. They reported higher $J_c$ values than we have obtained in our specimens, but direct comparisons are difficult owing to the fact that both Song and Mikheenko used an in situ processing method which tends to lead to higher grain connectivity [28].

To analyse flux pinning mechanisms, the field dependence of the flux pinning force density, $F_p = -J_c \times B$, has been evaluated at 20 K. Figure 8(a) shows the normalised pinning force density, $f_p = \frac{F_p}{F_{p,\text{max}}}$, for each sample as a

Table 5. Superconducting properties of the pure MgB$_2$ and composite bulk specimens.

| Sample  | $T_c$ (K) | $B_{irr}$ at 4.2 K (T) | $J_c$ at 4.2 K and 5 T (A m$^{-2}$) | $B_{irr}$ at 20 K (T) | $J_c$ at 20 K and 3 T (A m$^{-2}$) |
|---------|-----------|------------------------|-----------------------------------|----------------------|-----------------------------------|
| MgB$_2$ | 38.7      | 6.6                    | $5.2 \times 10^7$                | 3.8                  | $4 \times 10^7$                  |
| 0.5Ym1h | 38.1      | 6.6                    | $5.6 \times 10^7$                | 3.8                  | $3.9 \times 10^7$                |
| 0.5Ym12h| 37.7      | 7.6                    | $14 \times 10^7$                 | 4.1                  | $8.6 \times 10^7$                |
| 2Ym12h  | 37.2      | 7.2                    | $13 \times 10^7$                 | 4                    | $7.9 \times 10^7$                |
function of reduced field, $b = \frac{B}{B^*}$, where $B^*$ is the field where $J_r \to 0$. The $B^*$ values have been estimated using the method described by Martinez et al., which involves linear extrapolation of the low $J_r$ sections of the Kramer curves, $J_r B^*(B)$, ignoring the zone close to $B^*$ which is known to be strongly affected by flux creep [29]. Theoretical models of flux pinning based on the flux line shear mechanism predict that pinning curves take the functional form $f_p \propto b^p(1-b)^q$, with $p$ and $q$ values depending on the size and shape of the pins relative to the spacing of the flux line lattice and whether the pins are ‘normal’ material or weaker superconductor with a different Ginzburg Landau parameter ($\Delta\kappa$ pinning) [30].

For polycrystalline MgB$_2$ bulks, it is expected that the main pinning contributions will come from grain boundaries which give rise to ‘surface normal’ pinning ($f_p \propto b^p(1-b)^2$, $b_{\text{peak}} = 0.2$) and ‘point normal’ pinning ($f_p \propto b(1-b)^2$, $b_{\text{peak}} = 0.33$) presumably from small non-superconducting inclusions [31]. As can be seen in figure 8(a), the peak in the experimental flux pinning force curves for all three samples is at $b_{\text{peak}} \approx 0.25$, which is in-between the peak positions expected for ideal ‘surface normal’ and ‘point normal’ pinning. This suggests that the pinning mechanisms in all three samples is similar and has contributions from both surface and point pins. However, the shapes of the experimental curves differ from each other and the theoretical curves. In particular, the high field portion of the flux pinning curves, above $B_{\text{peak}}$ seems to get broader (and more similar to the theoretical curves) as the amount of Y$_2$O$_3$ increases. Figures 8(b)–(d) shows the fits of each experimental curve to a more general function $f_p = ab^p(1-b)^q$. The value of $p$ is reasonably consistent (1.1–1.6), but $q$ is found to increase with reducing doping concentration, with the undoped sample having $q > 4$, much higher than any of the standard models. This has been observed previously in polycrystalline MgB$_2$ and other superconductors and has been attributed to a wide distribution of superconducting properties ($B^*$) within the sample [29, 32]. This suggests that the undoped MgB$_2$ has rather inhomogeneous superconducting properties, and this improves upon doping with Y$_2$O$_3$.

In addition, careful inspection of the 2 wt% Y$_2$O$_3$ pinning curve shows evidence of a slight shoulder at around 0.5, which may indicate a slight contribution from another pinning mechanism such as ‘surface $\Delta\kappa$’, which theoretically has a peak at $b_{\text{peak}} = 0.6$.

4. Conclusion

Composite Y$_2$O$_3$–MgB$_2$ powders were successfully manufactured by mechanical alloying using high energy ball milling. XRD and STEM suggested that Y$_2$O$_3$ slowly dissolved into the MgB$_2$ matrix during mechanical alloying, by a process of Y$_2$O$_3$ dissociation so that Y and O showed a relatively uniform distribution at the nanoscale after 12 h of milling. Milled powders showed significant residual strains up to 0.5% and crystallite sizes of 50–100 nm. Bulk pellets were manufactured using FAST and presented a complex microstructure.
composed of a few hundred nanometres MgB2 grains and a fine dispersion of nanoscale YB4 and MgO precipitates. After only 1 h of milling, the YB4 dispersion was relatively inhomogeneous with large agglomerates at grain boundaries, whereas after 12 h of milling YB4 precipitates were 20 to 40 nm in diameter and more uniformly dispersed.

\[ \text{MgB}_2 + 0.5 \text{ wt% Y}_2\text{O}_3 \] (12 h) showed a significant improvement in \( J_c \) (4.2 K) at high field compared with unmodified MgB2, which was attributed to the relatively fine dispersion of nanoscale YB4 and MgO precipitates acting as efficient pinning centres. In contrast, MgB2 + 0.5 wt% Y2O3 (1 h) showed no improvement due to a coarser and more inhomogeneous microstructure. MgB2 + 2 wt% Y2O3 (12 h) had poorer superconducting properties, probably due to a reduction in grain connectivity caused by the large fraction of insulating precipitates located at grain boundaries. Adding Y2O3 slightly reduced \( T_c \) compared with unmodified MgB2, due to increased strain and defect concentrations that were not fully annealed out at 1150°C.

The ODS concept was successfully applied to superconductors and has provided a significant improvement in \( J_c \) at high field because of the precipitation of a fine dispersion of YB4 and MgO nanoparticles that acted as efficient pinning centres for magnetic vortices. Future work will explore additional processing parameters such as the sintering temperature and time in order to maximise the performance of these ODS superconductors by refining further their nanoscale microstructure.

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