Size reduction of boron particles by high-power ultrasound for optimization of bulk MgB$_2$

Sai Srikanth Arvapalli$^{1,}$, Muralidhar Miryala$^{1,}$, Milos Jirsa$^{2,}$ and Masato Murakami$^{1}$

$^1$ Superconducting Materials Laboratory, Graduate School of Science and Engineering, Shibaura Institute of Technology 3-7-5 Toyosu, Koto-ku, Tokyo 135-8548, Japan
$^2$ Institute of Physics ASCR, Na Slovance 2, Praha 8 CZ-18221, Czech Republic

E-mail: miryala1@shibaura-it.ac.jp

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Abstract

Critical current density, $J_c$, in superconductors is strongly connected with size of defects in the material. Frequently, the smaller defects, the higher $J_c$. In this work, we tried to reduce the size of cheap commercial boron precursor powder using high energy ultra-sonication in ethanol media. The resulting powder was then utilized in synthesizing bulk MgB$_2$ via sintering at 775 °C. Effect of boron powder ultra-sonication on superconducting properties of the bulk MgB$_2$ was studied and discussed. SEM of ultra-sonicated boron showed fine particles with sharp edges (high-energy surfaces), irregular shapes and clustering of fine particles occurred for longer ultra-sonication durations. XRD proved a high quality of MgB$_2$ with only small traces of MgO. Around 36% improvement in $J_c$ at 20 K and $T_c$ close to 39 K were observed in MgB$_2$ bulk prepared with boron ultra-sonicated for 15 min. Microstructure studies showed numerous nanometre sized MgB$_2$ grains in the bulk. Other bulks (made of boron ultra-sonicated longer, for 30, 45, and 60 min) have larger grains. It resulted in slightly lower $J_c$, anyway, still by 22% higher than in reference bulk. The present results demonstrate that the high performance bulk MgB$_2$ can be achieved without reduction in $T_c$ via employing a cheap boron, reduced in size by high-energy ultra-sonication.

Keywords: high energy ultra-sonication, sintering, bulk MgB$_2$, cheap commercial boron

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

1. Introduction

MgB$_2$ is a trendy material suitable for several superconductor applications such as bulk magnets for compact MRI & NMR, electric motors etc. Although $T_c$ is slightly lower (39 K) [1] compared to superconducting cuprates (~90 K), the processing time, easy fabrication and cost parameters make it attractive. With liquid helium cooling would be usage of MgB$_2$ difficult and expensive in practical applications. However, cryogen-free cryo-coolers [2–4], liquid hydrogen [5] and neon are capable of reaching the required cooling temperature without expensive and technically complicated use of liquid helium. This promotes a rapid research on MgB$_2$ superconducting material. The light weight is another factor improving efficiency of the devices and increasing the range of applications [6–11], especially in space. Several research groups have been trying to improve trapped field and critical current density in MgB$_2$ bulks. Most of the trials were related to optimization of synthesis parameters [12, 13], novel synthesis...
techniques [14–16], refining the raw precursors, doping, additions [17, 18], and fabrication of films [19]. The commonly used synthesis method for bulk MgB$_2$ is sintering. This process is highly scalable and by maintaining uniformity in synthesis parameters, one can obtain uniformity in product’s properties, such as elemental distribution, density, $J_c$ etc. In addition, this sintering method also ensures a uniform trapped field, which is crucial for levitation and super-magnet device fabrication. Some researchers have tried manipulating the sintering temperature, sintering duration, multi-step heating [20–23] etc. In our previous research we have optimized the sintering process such 775 °C–800 °C for 3 h for best performance bulk MgB$_2$ [12]. One small disadvantage is the need of an inert atmosphere during the sintering, as Mg is highly reactive with oxygen. Anyway, it does not hinder massive production of bulk MgB$_2$ material. Different techniques and synthesis methods were also practiced such as spark plasma sintering [24–26], diffusion method [16], infiltration growth [27] and chemical routes (combustion, pyrolysis, precipitation etc.). All these methods have their advantages and disadvantages. One way that can improve superconducting performance is to introduce pinning centers to pin vortex lattice motion and thereby reach a high performance up to high magnetic fields. The coherence length of MgB$_2$ materials is quite high when compared to other high temperature superconductors. Hence, defects with bigger sizes can thus act as pinning centers. Some of the effective pinning centers used are non-superconducting inclusions, defects, grain boundaries, voids etc. Such pinning centers can be MgB$_4$ [28, 29], MgO [30, 31], metals [32, 33], metal oxides [34, 35], grain refiners, rare-earth elements [36], dislocations, defects created by irradiation [37], carbon doping [38–45] etc.

It has been proven that increase of grain boundary density results in increase of $J_c$, in particular at low magnetic fields. In one our previous work dealing with MgB$_2$ we used a commercial nano-amorphous boron [46] to enhance vortex pinning. The results were outstanding, but the powder was

Figure 1. XRD of the ultra-sonicated boron based samples (B-0, B-15, B-30, B-45, B-60). All diffraction patterns showed no sign of B$_2$O$_3$ formation.
Figure 2. SEM micrographs of (a) B-0, (b) B-15, (c) B-30, (d) B-45, and (e) B-60 samples. Fine particles around a few nanometers size can be seen after ultra-sonication. In samples based on longer ultra-sonicated powders, clustering can be observed.

Figure 3. XRD of the samples B-0, B-15, B-30, B-45, and B-60. All diffraction patterns are similar to conventionally sintered MgB$_2$, with scarce MgO impurities.
and frequency at 20 kHz. The power was switched ON and OFF alternatively every 30 s. This ensured that the metal tip generating pulses got enough time to cool off the entire heat produced by the particles bombardment. Thus the real ultra-sonication times were 15, 30, 45, and 60 min. Immediately after the ultra-sonication, the powder was heated at 100 °C for one hour in a muffle furnace to remove ethanol. Later, the powders were characterized by SEM.

### 2.2. Synthesis of MgB₂

The precursors were commercial powders (Furuuchi Chemical Corporation) of amorphous Mg powder (99.9% purity, 200 meshes) and an ultra-sonicated boron powder. One gram of MgB₂ was synthesized using 0.529 g of Mg and 0.471 g of B (ultra-sonicated) in the molar ratio of 1:2. The powders were rigorously mixed and ground in a glove box to avoid oxidation. The mixture was then pressed into 20 mm diameter, 7 mm thick pellets using a uniaxial hydraulic press with a force of approximately 20 kN. These pellets were immediately wrapped in Titanium (Ti) foils and heat treated via sintering at 775 °C for 3 h in a tube furnace in Ar atmosphere. The pellets we then removed and outer surface is polished to avoid any surficial MgO formed. From here on we address the various MgB₂ bulks as B-0 (non-ultra-sonicated/pristine boron powder), B-15, B-30, B-45, and B-60, in correspondence with the used boron precursor, ultra-sonicated for 0, 15, 30, 45, and 60 min, respectively. Here B-0 means that boron was neither ultra-sonicated, nor soaked in ethanol.

### 2.3. Characterization of MgB₂

The constituent phases of the samples were identified with a high-resolution automated Rigaku smart-lab x-ray powder diffractometer (RINT2200-) with a step size of 0.01° from 10° to 90°, using Cu-Kα radiation generated at 40 kV and 30 mA. The microstructure of these samples was later studied by field emission scanning electron microscope (FE-SEM).

Superconducting critical temperature (Tc) and magnetization hysteresis loops (M-H) were measured using SQUID Magnetometer (Quantum Design, model MPMS5). Specimens for SQUID measurements, with approximate dimensions of 1 x 1 x 0.75 mm³, were cut from bulk MgB₂ samples. Jc was calculated from the M-H loops using the extended Bean critical state model formula for finite rectangular samples,

\[ J_c = 20\Delta m / \left[ a^2 c (b - a/3) \right] \]

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Figure 5. Superconducting critical current density as a function of magnetic field of the samples B-0, B-15, B-30, B-45, and B-60, measured at 20 K. All samples with ultra-sonicated boron, especially B-15, show improvement in $J_c$.

where $a$, $b$ are cross-sectional dimensions, $b > a$, and $c$ is thickness of the specimen ($a$, $b$, $c$ in mm). $\Delta m$ (in emu units, 1 emu = $10^{-3}$ Am$^2$) is the difference of magnetic moments during increasing and decreasing field in the $M$-$H$ loop.

### 3. Results and discussion

Ball milling as a standard technique for boron powder refinement is not suitable for industrial use because of the impurities, mainly B$_2$O$_3$ created during this process. XRD analysis revealed that the amount of B$_2$O$_3$ raised with increasing milling time, which resulted in a decrease of $T_c$ of the MgB$_2$ bulk [48]. The ultra-sonication process does not show such a drawback. XRD results proved absence of B$_2$O$_3$ diffraction peaks even after 1 h of ultra-sonication (100% intensity peak-usually at approx. $2\theta = 27.8^\circ$), as shown in figure 1. Note that any oxides in the precursor promote formation of MgO, which is detrimental to the superconducting properties. The particles size was studied by means of SEM. Figures 2(a–e) show the SEM micrographs of pure and 15, 30, 45, and 60 min ultra-sonicated boron. The particles size was significantly reduced with ultra-sonication. In addition, clustering or agglomeration can be observed in boron powder ultra-sonicated for longer time than 15 min, especially in B-30, B-45, and B-60 as pointed in the figures 2(c–e), respectively. Refinement up to few tens of nanometers was observed. This implies that although there is size refinement with increasing ultra-sonication time, longer intervals than 15 min result in a particles clustering, due to intensive particle collisions during the processing. We propose that the particles after 15 min of bombardment end up with irregular surfaces and smaller sizes, and further collisions can lead to interlocking of particles. Another possible explanation can be agglomeration, which is mainly due to the tendency of the system to minimize surface energy [51]. Similar phenomenon was reported recently, when boron was subjected to ball milling for size reduction [48]. The authors concluded that after 2 h of ball milling, the performance goes down because of volume reduction in MgB$_2$ phase. They also observed formation of unreacted Mg and B$_2$O$_3$. In the case of ultra-sonication, very minute amount of MgO was observed and $TModel
Figure 6. FE-SEM images of (a) B-15, (b) B-30, (c) B-45, and (d) B-60 samples. Note the agglomerated tiny B particles grown into large grains in longer ultra-sonicated boron based bulk MgB$_2$.

reference MgB$_2$. Ultra-sonication occurs to be better than ball milling in terms of balanced quality, performance, and processing time.

From the XRD shown in figure 3 it is evident that there are no contaminants present in the matrix apart a scare quantity of MgO, which is formed during the transfer from glove box to furnace and the pressing step. The intensity of MgO [220] peak (2θ ~ 62.3°) can be seen in the inset figure. Compared to other peaks, it is very small. In addition, we compared the [110] MgB$_2$ peak (2θ ~ 60°), to check if there was any influence of ethanol such as carbon contamination during ultra-sonication. In general, carbon substitutes boron ions at boron atomic places, which are parallel to $c$-axis. Hence, we chose [110] plane to determine any carbon substitution. As can be seen from the inset of figure 3, there was no shift in the [110] peak, which confirms that there was no carbon substitution.

In accordance with XRD, $M$-$T$ or superconducting critical temperature studies also show a sharp transition, which depicts the high quality bulk MgB$_2$ synthesis. All the samples show high $T_{\text{conset}}$ such as 38.5 K and $\Delta T_c$ around 0.7 K, more details can be found in table 1 and figure 4. These results also point to a high purity, as most of the secondary phases present in a superconducting material result in degradation of critical temperature. Additives and dopants such as carbon in various forms, Ti, Cu, Fe, SiC and others resulted in great decrease in $T_c$ [45, 52–56]. In figure 5, the critical current density as a function of magnetic field was plotted in semi-log plots, along with regular curves in the inset. One can see that B-15 is the best, both in $J_c$ and $H_{\text{irr}}$. Self-field $J_c$ at 20 K raised up to 300 kA cm$^{-2}$ in B-15 bulk, while all other samples based on boron ultra-sonicated for longer times exhibited nearly same self-field $J_c$, close to 270 kA cm$^{-2}$. Thus, there is about 36% improvement in B-15 and 22% improvement for B-30, B-45, and B-60 when compared to B-0 (220 kA cm$^{-2}$). In order to understand this improvement, we carried out several microstructural studies using FE-SEM. From figures 6(a–d), we can observe that the particles in B-15 bulk microstructure are slightly finer than in other bulks. This is because the clustered boron particles during ultra-sonication resulted in formation of larger MgB$_2$ grains in B-30, B-45, and B-60 bulks, which in turn reduced the grain boundary density. Figure 7 reveals the average particle sizes of these bulks’ microstructures. B-15 bulk has an average particle size of 260 nm, while B-30, B-45 and B-60 have 320, 350, and 370 nm, respectively. As we know, grain boundaries are primary pinning centres in bulk MgB$_2$ superconducting systems. Hence, the $J_c$ reduction with the longer durations of ultra-sonication is a result of agglomeration or clustering of nanoscopic B particles. During liquid-solid reaction of Mg with B fine MgB$_2$ particles dissolve in the Mg melt and contribute to growth of bigger crystallites [57]. From these results, we can comprehend that the system reaches optimum at 15 min of B ultra-sonication. Similar technique can be applied to fabrication of wires and tapes. The prior research on wires (Ag sheathed MgB$_2$–750 °C/5 h) showed a critical current densities of around $2 \times 10^4$ A cm$^{-2}$, which is much less compared to our present bulk $J_c$ values [58]. It shows that ultra-sonication of B powder can find its prospects also in wire fabrication.
To observe the effect of ultra-sonication on pinning mechanism, we calculated flux pinning diagrams. The results were evaluated in terms of Dew-Hughes general expression [59],

\[ f_p = A(h)^p (1 - h)^q \]  (2)

where \( f_p \) is normalized flux pinning force, \( f_p = F_p/F_{p,max} \), and \( h \) is reduced magnetic field, \( h = H/H_{irr} \), where the irreversibility field, \( H_{irr} \), was determined as the field, where \( J_c \) in the \( J_c(H) \) dependence fell down to 100 A cm\(^{-2} \), a standard practice in our works. The \( f_p(h) \) dependence was analysed at 20 K. The dependence of equation (2) exhibits one peak at the field \( H_{max} \). Dew-Hughes correlated the peak positions with different types of pinning in the material. In our case, the peak position of most samples was located at 0.21 (see figure 8), close to the position 0.2 predicted by Dew Hughes for grain boundary pinning (\( \delta \) pinning). This result was expected because we only reduced size of raw material (boron), increasing the grain boundary density. In fact, grain boundary pinning is a standard pinning mechanism observed in sintered bulk MgB\(_2\) superconductor systems to which our samples belong. While all ultrasonicated samples exhibited the peak at \( h \approx 0.21 \), the conventionally prepared MgB\(_2\) bulk had the peak at \( h \approx 0.19 \). This difference is marginal and is comparable to experimental error in determining \( B_{irr} \). It can be also affected by other factors discussed further. The most significant difference was obviously in the curve width. We tried to model the experimental data by Dew Hughes expression, equation (2), with free parameters \( p, q \), and \( A \). From the fit, we obtained \( p \approx 0.7, q \approx 2.6 \), and \( A \approx 5.503 \pm 0.01 \). The fit curve in figure 8 is displayed in green colour and labelled as Fit equation (2). The fit curve perfectly imitates flux pinning diagrams of all the bulk samples. Both the fit curve and the experimental ones are rather slender compared to the original theoretical curve of grain boundary pinning [59], with \( p = 0.5 \) and \( q = 2 \) (the dark cyan curve labelled as Ref in figure 8). This procedure has the only drawback that it lacks any theoretical background. In the polycrystalline bulk MgB\(_2\), factors such as anisotropy and current percolation play important roles that can significantly slenderize the curve [60]. In addition, there might be effect of magnetic relaxation resulting in a difference between \( H_{c2} \), to which magnetic fields in the original model were reduced, and irreversibility field, \( H_{irr} \), determined by equilibrium between flux pinning and magnetic induction.

SEM images of the ultra-sonication based bulks revealed tiny nano-sized particles at pore surfaces, which might act
Figure 8. Flux pinning diagram of ultra-sonicated samples (B-0, B-15, B-30, B-45, and B-60) with curve fitting by theoretical expression for grain boundary pinning (Ref) compared to the fit by the same formula but with $p$ and $q$ left free for fitting (equation (2)). Peak positions around $h \sim 0.2$ of all samples confirm dominance of grain boundary pinning.

as point pinning centres (see figure 9). A similar effect was observed in MgB$_2$ bulk system also by some other authors [61, 62]. We tried to incorporate point pinning into the pinning diagram analysis but its role appeared to be marginal in the pinning diagram, therefore we do not show the results here.

In order to check the potential use in applications, we measured $J_c$ of the best sample (B-15) at temperatures ranging from 10 K–35 K. High self-field $J_c$ such as 434 and 382 kA cm$^{-2}$ was observed at 10 K and 15 K, respectively (see figure 10).

4. Conclusion

A novel high energy ultra-sonication technique was applied on cheap commercial boron precursor to improve superconducting performance of sintered bulk MgB$_2$. We successfully refined boron up to nanometer size without formation of B$_2$O$_3$. Longer ultra-sonication resulted in clustering of boron particles and deterioration of electromagnetic properties. XRD and magnetic studies of bulk MgB$_2$ fabricated with this powder showed no impurities and high quality ($T_c \sim 38.5$ K; $\Delta T_c \sim 0.7$ K). $J_c$ improvement by about 36% was observed for an optimized regime of MgB$_2$ preparation. According to our study, 15 min of boron ultra-sonication in ethanol is optimal for the best MgB$_2$ performance and reaches saturation thereafter because of formation of larger grains in the matrix. $J_c$ as high as 434, 382, and 280 kA cm$^{-2}$ was achieved in MgB$_2$ bulk prepared of for 15 min ultra-sonicated boron (B-15) at 10 K, 15 K, and 20 K, respectively. Flux pinning studies indicated that dominant pinning was grain boundary pinning, typical for MgB$_2$ systems. Small nanosized particles were formed on pore surfaces, presumably
MgO or Mg-B-O, that might act as point pinning centres. Anyway, the effect of point defects on the total pinning force density is negligible. The ultra-sonication technique is highly cost effective, impurity free, and scalable and thus suitable for transfer of bulk MgB$_2$ material to practice.

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ORCID iDs

Sai Srikanth Arvapalli https://orcid.org/0000-0001-5063-4683
Muralidhar Miryala https://orcid.org/0000-0003-2205-0378
Milos Jirsa https://orcid.org/0000-0001-8685-5998

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