Pinning behavior in bulk MgB$_2$ prepared using boron powder refined via high-energy ultra-sonication

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Abstract
We successfully refined cheap commercial boron powder by means of high-energy ultra-sonication and utilized it in synthesis of bulk MgB$_2$. Rietveld phase analysis of X-ray diffraction pattern revealed completely formed MgB$_2$ with a low amount of MgO. MgB$_2$ bulk prepared of boron ultra-sonicated in ethanol for 15 min showed self-field $J_c$ of around 300 kA/cm$^2$ at 20 K without any compromise in $T_c$ (~39 K). Pinning analysis based on Dew-Hughes expression showed major pinning contribution from grain-boundary pinning (~95.5%), along with a slight contribution from point pinning (4.5%). The microstructure study detected a system of large MgB$_2$ grains (hundreds nm large) and 10–20 nm sized particles, possibly Mg-B-O, formed at MgB$_2$ grain boundaries.

Keywords Flux pinning · Bulk MgB$_2$ · Boron refinement · Ultrasonication

1 Introduction
Superconductivity in MgB$_2$ was discovered by Jun Akimitsu et al. in 2001 [1]. Since then, a huge amount of research on the material was done all around the world. Due to uniform trapped field, and cheap and simple processing, MgB$_2$ is suitable for several superconductor applications such as bulk magnets for compact MRI and NMR, electric motors, etc. [2–4]. Furthermore, its light weight is an important feature that might be crucial for some applications, especially space ones [5]. Although $T_c$ is lower (39 K) compared to cuprates (YBa$_2$Cu$_3$O$_{7-\delta}$ ~ 93 K [6], Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ ~ 105 K [7], etc.), the processing time is shorter and fabrication is easy. These features make the material attractive for mass production and device design. Despite these great advantages, $J_c$ of MgB$_2$ is only moderate and the compound cannot be cooled into superconducting state by liquid nitrogen. It also exhibits a poor volume density when prepared via conventional sintering. Numerous studies are in progress to address these issues to make MgB$_2$ commercially attractive. Density can be highly improved via high-pressure techniques such as spark plasma sintering and hot isostatic pressing. While the low $T_c$ prevents use of common and cheap liquid N$_2$ for MgB$_2$ cooling, instead of the expensive liquid He, one can use the moderately priced liquid Ne (27 K) or H$_2$ (23 K). Cryogen-free cooling technique has also been recently developed, reaching just the temperature range of MgB$_2$ superconductivity [8]. An extensive research was also done to improve $J_c$ of MgB$_2$ bulk superconductors. The main factor for improving $J_c$ is flux pinning strengthening. In general, defects close to coherence length of the superconducting matter act as flux pinning centers, usually dislocations, lattice defects, etc. Compared to cuprates, MgB$_2$ has a large coherence length and therefore grain boundaries act as prominent flux pinning centers. In our earlier works, we studied the phase diagrams and optimized sintering time and temperature for obtaining finer MgB$_2$ grains while avoiding all unreacted precursors [9]. This fine-grained matrix showed improved $J_c$ due to a higher grain boundary density—more flux pinning centers in the matrix. Elsewhere, $J_c$ was improved by adding dopants that either refined the microstructure or acted as flux pinning centers themselves. Variety of dopants was used such as metals, oxides, and carbon sources [10–18]. Of all the dopants, carbon showed the highest increment due to its...
substitution into boron sites. In our recent studies, we used a commercially prepared amorphous nano-boron precursor, which resulted in huge $J_c$ improvement [19]. This study showed that the boron precursor morphology hugely influences the final microstructure of sintered MgB$_2$ bulk and has a strong dependence on grain boundary pinning. Later, we have used carbon-encapsulated boron precursor, which is an amorphous nano-boron coated with carbon [20]. The MgB$_2$ bulk produced from this precursor showed huge $J_c$ improvement at self-field as well as at high fields. However, these commercial powders are three times more expensive than the conventional boron. The same effect, without using expensive precursors, was finally achieved by employing high-energy ultra-sonication (HEU). This technique is used to refine the regular conventional boron into nano-sized particles.

In the present work, we discuss the effect of HEU-processed boron on the final microstructure of MgB$_2$ bulk and its implications on $J_c$ and flux pinning properties. HEU with 50% power was used to refine boron for 15 min that ultimately resulted in 36% $J_c$ improvement. A peculiar microstructure was also observed, which revealed various pinning centers.

2 Fabrication and characterization

Regular conventional boron (Furu-uchi Chemicals, 300 mesh) was ultra-sonicated in ethanol for 15 min and used to fabricate sintered bulk MgB$_2$. Details of boron ultra-sonication can be found elsewhere [21]. Mg powder and HEU boron powder were mixed in a glove box in argon atmosphere. Later, the mixture was pelletized and sintered in tube furnace (in Ar flow) for 3 h at 775 °C. The processed bulks were characterized with Rigaku SmartLab X-ray powder diffractometer (XRD-RINT2200), Rietveld analysis of the refined phase fraction using diffraction (MAUD) software, field-emission scanning electron microscope (FESEM – JEOL/JSM-7100F), and superconducting quantum interference device (SQUID magnetometer - Quantum Design, model MPMS5). Furthermore, extended Bean critical state model formula was used to estimate $J_c$ and Dew-Hughes expression was used to model the flux pinning diagrams [22].

3 Results and discussion

XRD of HEU boron shows no signs of B$_2$O$_3$ phase, which promotes MgO phase that is detrimental to superconductivity of MgB$_2$ bulk [21]. The average size of boron powder before ultra-sonication is a few microns, while after the ultra-sonication is sub-micron to a few hundred nanometers. Simultaneously, XRD of MgB$_2$ bulk also shows a very low amount of MgO impurity. Rietveld phase fraction analysis of the bulk showed only 3.6 wt% of MgO, which is less than
what we observed in conventional MgB$_2$ before (Fig. 1). The differential susceptibility vs temperature curves show that all the bulks have $T_{c_{onset}}$ close to 38.5 K and the transition width (calculated from the width of peak of $d\chi/dT$ curves), $\Delta T_c$, is for all the bulks about 0.7 K (Fig. 2) which indicates high quality of the fabricated bulks. The critical current density was calculated using the extended Bean critical state model. Figure 3 shows the superiority of HEU-based bulks’ $J_c$ over conventional bulk at various fields. Fifteen minutes of ultra-sonication is best for obtaining high-performance MgB$_2$ bulk. The self-field $J_c$ value was around 300 kA/cm$^2$, by 35% more than in a normal bulk—220 kA/cm$^2$ [21]. Longer ultra-sonication resulted in boron agglomeration that led to large MgB$_2$ grains reducing $J_c$. A more detailed explanation can be found elsewhere [21].

Flux pinning diagrams were estimated to determine the pinning mechanism, using Dew-Hughes general expression [23]:

$$f_p = A(h)^p(1-h)^q$$  

where the normalized flux pinning force density is $f_p=F_p/F_{p,max}$ and the reduced magnetic field is $h=H/H_{irr}$. The irreversibility field, $H_{irr}$, was determined as the field where $J_c$ fell down to 100 A/cm$^2$, a standard practice in our works. Dew-Hughes suggested that the peak position of $f_p(h)$ dependence indicates the type of pinning in the material. In terms of this model, peak position at 0.2 implies grain boundary pinning, at 0.33 implies $\delta T_c$ pinning, etc. In the MgB$_2$ bulks, we observed the peak position located at 0.22 (Fig. 4), slightly above 0.2. In one of our earlier works, where amorphous nano-boron was used, the grain boundary density intentionally increased resulting in a huge boost in self-field $J_c$. In addition, the $f_p(h)$ peak position was around 0.17, which signified full responsibility of grain boundaries for vortex pinning [19]. On the other hand, when carbon-encapsulated boron was used, the peak position shifted to 0.23, likely due to defects and strain created by carbon substitution [20]. From these two scenarios, it can be postulated that when grain boundaries are sole contributors of flux pinning, the peak position shifts toward lower $h$ values (< 0.2) and when other forms of pinning are active, the peak position shifts to the higher values (> 0.2). This also justifies why grain boundaries are known as low-field pinning centers in MgB$_2$ superconducting system. In the above context, since the peak position of present MgB$_2$ bulk prepared from ultra-sonicated boron is above 0.2, we believe that the flux pinning is mostly from grain boundaries but slightly affected by another pinning mechanism.

In the same bulk, we previously tried to fit the experimental curve by Eq. (1) with free pinning parameters ($p$, $q$), which led to the values $p \sim 0.7$, $q \sim 2.6$, different from any of the theoretical settings. We also tried to correlate microstructure with pinning mechanisms. FE-SEM images showed two different types of microstructure. One with refined MgB$_2$ grains with dimensions up to 100 nm, which make up the majority of matrix, and numerous 10–20-nm-sized particles at the pore surfaces (Fig. 5). We consider these tiny nano-particles to be Mg-B-O, which was observed previously in the MgB$_2$ bulk system [24]. These particles are usually formed when boron dissolves in MgO or reacts with Mg and oxygen, forming a solid solution during sintering at a high sintering temperature. The morphology of the Mg-B-O phase usually varies with temperature. Depending on the sintering temperature, the Mg-B phases are formed as 5–20-nm-thick layers or 5–10-nm particles [25]. These microstructural evidences inspired us to think that these tiny nano Mg-B-O particles might contribute to pinning. We tried to calculate the contribution of point pinning in addition to conventional grain boundary pinning by using the expression suggested by Koblishka et al. [26]:

**Fig. 3** Critical current density ($J_c$) of various HEU boron-based MgB$_2$ bulks at magnetic fields of 0, 0.5, and 1 T, 20 K

**Fig. 4** Flux pinning diagram of 15 min HEU boron-based MgB$_2$. Peak position slightly shifted right
\( f_p = w^* \left[ A_1 (1-h)^{p1} + (1-w)^* \left[ A_2 (1-h)^{q2} \right] \right] \) (2)

\( p1 = 0.5 \) and \( q1 = 2 \) (grain boundary pinning), \( p2 = 1 \) and \( q2 = 2 \) (point pinning), \( A_1 \) and \( A_2 \) being constants, and \( w \) a weight factor. By fitting the experimental data for 15 min ultra-sonicated MgB\(_2\) with Eq. (2), we arrived at \( A_1 \sim 3.6 \), \( A_2 \sim 3.2 \), and \( w \sim 0.9545 \) that indicated that nearly 95.5% of pinning came from grain boundaries, with the rest (4.5%) being point pinning. This is probably the reason for the slight shift in the peak position. The contribution from point pinning is very low, due to formation of nano-Mg-B-O particles only on the pore surfaces rather than inside the matrix. The model curve (blue) in Fig. 4 is slightly broader than both experimental curves. The reason is that the theoretical model did not take into account anisotropy and other factors associated with the polycrystalline nature of MgB\(_2\) bulks [27].

4 Conclusion

The high-energy ultra-sonication is a cost-effective way to refine boron, which hugely improves \( J_c \) of MgB\(_2\). The superconducting bulk quality is very high, as evidenced by the Rietveld phase fraction analysis of XRD patterns and by the low peak width of the differential susceptibility curves. Bulk matrix consists of MgB\(_2\) particles with dimensions around 500–100 nm. Flux pinning diagrams revealed that the majority of flux pinning is from grain boundaries. Detailed assessment of flux pinning diagrams revealed a little contribution from point pinning as well. Micrographs identified numerous nano-sized Mg-B-O particles on the pore surfaces, which might cause the slight shift of the peak in the flux pinning diagram (Fig. 4) towards values higher than 0.2.

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