Processing and Characterization of Charcoal Added Bulk MgB₂ Superconductor

J Longji Dadiel¹*, M Muralidhar¹*, Sai Srikanth Arvapalli¹, S Pavan Kumar Naik¹,² and M Murakami¹

¹Superconducting Material Laboratory, Graduate School of Science and Engineering, Shibaura Institute of Technology, 3-7-5 Toyosu, Koto-ku, Tokyo 135-8546, Japan
²Electronics and Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Central 2, Umezono, Tsukuba, Ibaraki, 305-8568, Japan

*miryala1@shibaura-it.ac.jp / mg17009@shibaura-it.ac.jp

Abstract: In this study, we focus on methods to further improve the flux pinning and critical current density (Jc) of disk shaped MgB₂ bulk superconductors by a comparative study with locally obtained charcoal at optimized processing conditions. The doping of charcoal was varied at 0, 0.2, 0.4 and 0.6 wt%. Bulk MgB₂ samples were produced by in-situ solid state reaction in Ar gas and ambient pressures at 775 °C, employing high purity of Mg metal and nano B powder mixed in a fixed ratio of Mg:B = 1:2 and optimal conditions. The phase has been investigated by X-ray diffractometer (XRD). The effects of the dopants on superconducting properties especially the field dependence of Jc have been determined by superconducting quantum interference device (SQUID) and critical temperature (Tc). Measurements of the magnetic susceptibility showed sharp superconducting transitions (∆Tc ~ 1 K). Jc at self-field and 20 K was determined to be ~280 and 467 kA/cm² for the 0 and 0.4 wt% charcoal added samples respectively. The structural and superconducting results were correlated with the addition of charcoal in the final product.

Keywords: MgB₂; charcoal; X-ray diffraction; critical current density, flux pinning, scanning electron microscope

1. Introduction

The discovery of superconductivity in MgB₂ is one of the most intriguing achievements owing to its relatively high critical temperature (Tc of 39 K) compared to the conventional low-temperature superconductors like Nb₃Sn, NbTi. MgB₂ offers the possibility of wide engineering applications in the temperature range 20-30 K, where Nb₃Sn and Ni-Ti alloy are not applicable due to their low Tc. Further, the field trapping capability for the practical applications of bulk MgB₂ magnets is similar to melt-textured REBa₂Cu₃Oₓ, which can be utilized as a trapped field magnet in nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) [1-6]. Considerable efforts have been made to improve the critical current density (Jc), upper critical field (Hc₂), and irreversibility field (Hir) of this superconductor [7]. Also, significant progress has been made concerning the development of processing techniques, improving the flux pinning, and large size MgB₂ bulk growth [1-5]. To utilize this material for industrial applications, including superconducting super-magnets, a further
improvement of $J_c$ is crucial, especially in sintered bulks [6, 8]. Doping of elements or compounds have been found to be effective for improving the superconducting properties of bulk, tapes, wires, and films, especially under magnetic fields [9]. Several approaches have been developed for incorporating the effective flux pinning centers in bulk MgB$_2$ material in-order to improve the superconducting performance. In high magnetic fields MgB$_2$ exhibits a decrease in $J_c$, due to its poor grain connectivity and lack of strong pinning centers. Earlier studies indicated that an inclusion of nano-dopants enables control of MgB$_2$ microstructure by introducing nano-pinning centers into the superconducting matrix. Among several substitutions, carbon doping is found to be effective [10].

In our previous work, we investigated the effect of nanoscopic diamond particles addition on bulk MgB$_2$ material by means of X-ray diffraction (XRD), superconducting transition temperature and critical current density at 20K [11]. The optimal amount nanoscale diamond addition to MgB$_2$ makes it possible to form a high density of nano-inclusions in MgB$_2$ matrix and improved the $J_c$ dramatically. However, to reduce the cost of production one must look for the naturally available other form of carbon sources. To improve the pinning performance of bulk MgB$_2$ materials, we tried to utilize other form of carbon sources such as activated charcoal in combination with optimum sintering temperature set in earlier studies [6]. Due to its low cost, we have selected charcoal as a carbon source for a carbon-doped MgB$_2$, studied the variation of $T_c$, triggering of different phases and $J_c$. The best sample indicated a high critical current density around 467 kAcm$^{-2}$ at 20 K and the superconducting transition temperature around 37.5 K.

2. Experimental details

The MgB$_2$ samples with the varying contents of charcoal were synthesized by an in situ liquid-solid reaction. The starting powder materials were Mg powder (99.9% purity, 325 mesh), nano sized amorphous boron powder (98.5% purity, ~250 nm), and locally obtained charcoal powder from charcoal market, Plateau raiders, Jos-Nigeria as dopant. The charcoal powder was collected and pulverized at the mineral processing department of the National Metallurgical Development Centre Nigeria. Ball milling was carried out employing BICO made (395-50 model, 220 V, 3ph, 60 cycles) with ball (3/4 inch - 1½ inch) to powder ratio of 10:1. The precursors were pressed into pellets of 10 mm in diameter and 7 mm thickness by use of a uniaxial press. The samples were sealed in titanium foils and then sintered at optimal temperature of 775 °C for 3 h in a tube furnace under pure argon atmosphere prior to cooling to room temperature [6]. The crystal structures and constituent phases of the fabricated MgB$_2$ samples were investigated using a high-resolution X-ray powder diffractometer (Rigaku/SmartLab), using Cu-K$_a$ radiation ($\lambda = 1.5418$ Å). The XRD patterns were collected with a step size of 0.02° over a 20 range from 20° to 90°. The microstructural properties were investigated employing field emission scanning electron microscopy (FESEM, Jeol JSM-7100F model). Temperature and field dependent characterization of the samples was conducted by subjecting smaller specimens of dimension ~2.0x2.0x1.0 mm$^3$ from the sintered pellets using a SQUID magnetometer (MPMS5). The $J_c$ values were estimated from the magnetization hysteresis loops (M-H loops) swept from 0 to 5 T at a constant temperature of 20 K based on the modified Bean critical state model:

$$J_c = \frac{20\Delta m}{a^2d(b-a/3)} \text{ (A/cm}^2\text{)}$$

where $d$ is the sample thickness, $a$ and $b$ are the cross-sectional dimensions (in mm) with $b \geq a$, and $\Delta m$ is the difference of the magnetic moments (in emu) during increasing and decreasing field in M-H loop [12]. The critical temperatures were also determined by magnetic susceptibility measurements from the onset of diamagnetism.

3. Results and discussion

Further, the charcoal powder was sieved and ball milled for 2 hours down to from <40 to 160 nm particle size as analyzed using the zeta potential particle analyzer. In figure 1, the obtained size distribution histogram of the charcoal powders is presented which shows that the particles are distributed majorly in the size range of 60-100 nm. The Mg and B powders were mixed in the nominal
ratio of 1:2 while varying the compositions of the charcoal for each sample produced at 0, 0.2, 0.4 and 0.6 wt% under argon atmosphere in a glove box.

Figure 1. Charcoal particles size histograms as obtained from the Zeta potential measurement after sieving and ball milling.

Figure 2 shows the XRD patterns of all synthesized MgB$_2$ samples, which gives the information on the crystallographic phases at different levels of charcoal doping. All the major Bragg peaks of MgB$_2$ hexagonal structure can be identified, indicating that samples mainly consist of the desired MgB$_2$ phase with minimal amount of MgO reflecting in all samples as impurity. The formation of MgO could not be completely prevented due to high reactivity of magnesium with oxygen, we were able to observe only MgO impurity by XRD, similar to our reports [13]. The lattice constants were evaluated from the XRD results which indicate little strains in direction of higher angles as shown in Table 1. The slight variation in the lattice constants is an indication that the amount of C-doping from the charcoal was effective in causing a small lattice distortions indicating minute C substitution in samples. Whereas, the c lattice constant is ~3.525 Å and is almost invariant. These results are similar to previous reports available with lowest C-doping in MgB$_2$ samples [14-15]. The effective C substitution (C$_{\text{eff}}$) in MgB$_2$ samples was determined using the relation described in the previous literature [16]. It was found that the C$_{\text{eff}}$ values are ~0.007 which confirms to the chemical formula of the ~MgB$_{1.993}$C$_{0.007}$.

Figure 2. (a) X-ray diffraction patterns of charcoal doped MgB$_2$ bulk samples produced using the mixture of the nano boron powders and different charcoal contents in sintering process
No particular shift in Bragg peaks was observed in XRD which reveals that considerable amount of substitution has not happened and not to mention the added charcoal was very minute. However, as usual slight MgO impurity phase formation can be seen.

Table 1. Starting compositions, lattice constants, onset and offset $T_c$’s compared with the changing transitions

| Sample | Nominal ratio | Lattice parameters ($a$ (Å), $c$ (Å)) | Superconducting transition (K) |
|--------|---------------|---------------------------------------|---------------------------------|
|        |               | $T_{c,\text{onset}}$ | $T_{c,\text{zero}}$ | $\Delta T_c$ |
| Reference | MgB$_2$ + 0 wt% Charc | 3.0864, 3.5253 | 38.3 | 37.9 | 0.4 |
| 1      | MgB$_2$ + 0.2 wt% Charc | 3.0836, 3.5253 | 37.9 | 37.2 | 0.7 |
| 2      | MgB$_2$ + 0.4 wt% Charc | 3.0834, 3.5248 | 38.0 | 37.2 | 0.8 |
| 3      | MgB$_2$ + 0.6 wt% Charc | 3.0834, 3.5248 | 37.9 | 36.5 | 1.4 |

The DC magnetic susceptibility curves were measured on the MgB$_2$ samples with a varying content of the charcoal powder in a magnetic field of 1 mT. All samples show sharp superconducting transitions (with transition width $\Delta T_c$ of ~ 1 K). There was a slight change in the onset of the critical temperatures ($T_{c,\text{onset}}$) with inclusion of charcoal (Fig 3, left). Here we obtained the $T_c$ onset around 37.9 K for 0.6 wt% of charcoal as compared to high $T_c$ onset of 38.3 K for pure sample. More details regarding $T_c$ can be found in Table 1. This could indicate that we have to find an optimum between possible superconductivity degradation and pinning enhancement [11]. The temperature dependence of the shown magnetization curves indicated that the onset of $T_c$ for the charcoal added samples is slightly lower than that of the pure sample. In a typical carbon doped MgB$_2$, the $T_c$ is known to be dependent on the amount of carbon substitution into the boron sites which means that the more carbon substitution corresponds to a lower $T_c$ [17]. However, our results showed very little $T_c$ degradation which might be because of MgO and possibly the lower content of charcoal addition and small amount of effective C substitution as supported from the XRD results.

![Figure 3](image-url)  
Figure 3. Superconducting transition in the bulk MgB$_2$-charcoal produced using the mixture of the amorphous boron powders in sintering process (left). The field dependence of the critical current densities for charcoal added MgB$_2$ at $T = 20$ K (right). All samples are sintered at 775 °C for 3h in argon atmosphere.

The variation of the $J_c$ at 20 K as the function of the applied magnetic field was analyzed to investigate the effect of charcoal addition. Figure 3 (right) shows the $J_c$ curves at 20 K as a function of
applied magnetic field for the bulk MgB$_2$ material with varying content of charcoal powder. The self-field $J_c$ values of 0, 0.2, 0.4 and 0.6 wt% charcoal added MgB$_2$ samples are 280, 366, 467 and 341 kA/cm$^2$ respectively. The self-field critical current density around 467 kA/cm$^2$ was observed at 20 K for the best sample as compared to the $J_c$ of 280 kA/cm$^2$ for the pure sample. MgB$_2$ sample with 0.4 wt% of charcoal powder showed higher critical current density than the 0 wt% charcoal added MgB$_2$ as well as the other variables indicating the optimal composition among the present series. If the $J_c$ values are compared at 1 T applied field for 0, 0.2, 0.4 and 0.6 wt% charcoal added MgB$_2$ samples are 164, 201, 280 and 183 kA/cm$^2$ respectively. We can say that optimization was effective for the 0.4wt% charcoal added sample. To understand the mechanism for the improved superconducting performance we tried to test the microstructure. Similarly, high $J_c$ results were obtained previously with carbon coated boron which has high carbon content where the substitution can be seen clearly [18].

![Figure 4. High magnification FE-SEM images for the (a) 0 and (b) 0.4 wt% charcoal added MgB$_2$ samples](image)

Figure 4 shows the higher magnification FE-SEM images recorded on the fractured surface of 0 and 0.4 wt% charcoal added MgB$_2$ samples. From the keen observation of micro-structural features, it is evident that the 0.4 wt% charcoal added sample contain fine sized grains compared to former sample. The elementary pinning force in MgB$_2$ is dependent on its nano-structural control. $J_c$ at low field is simply determined by the grain connectivity, grain sizes and pinning force of the grain boundaries [19]. The results of the microstructural analysis show the presence of refined grains in the charcoal added sample and we emphasize that these grains aid in enhancing the $J_c$. These refined grains are possibly created by nano-sized charcoal particles and create strong pinning effects which are responsible for the improved flux pinning. The superconducting $J_c$ is highest in the 0.4 wt% charcoal added sample and we think that this may be because of the optimal distribution of refined grains.

4. Conclusions

MgB$_2$ bulk samples were successfully synthesized by a solid state sintering process and various amounts of charcoal addition. XRD studies indicated that all samples were single phase MgB$_2$ along with a small quantity of MgO. All the charcoal added samples showed a sharp superconducting transition around 38 K. The occurrence of superconductivity is slightly affected by the charcoal addition compared to pure MgB$_2$ materials. The effective grain refinement supported superior $J_c$ performance in 0.4 wt% charcoal added sample. Among all additions, 0.4 wt% charcoal was found to be optimal for superior field dependency of $J_c$ value of 467 kA/cm$^2$ at 20 K in self-field and 280 kA/cm$^2$ at 1 T. This work shows that addition of charcoal particles is a promising way to improve the superconducting performance of the MgB$_2$ bulk materials along with reducing the economic cost via cheap and abundant charcoal additive.
Acknowledgments
The paper was supported by Grant-in-Aid FD research budget code: 112261, Shibaura Institute of Technology (SIT). Longji would also like to thank the Japan International Cooperation Agency (JICA) for financial support through the ABE Initiative program. Thanks to Prof. Tetsuo Oka for continued support and advice.

REFERENCES
1. Vinod K, Abhilash Kumar R G and Syamaprasad U 2007 Supercond. Sci. Technol. 20 R1.
2. Perini E and Ginuchi G 2009 Supercond. Sci. Technol. 22 045021.
3. Kajikawa K and Nakamura T 2009 IEEE Trans. Appl. Supercond. 19 1669.
4. Gunchi G, Ripamonti G, Cavallin T and Bassani E 2014 Cryogenics 46 23.
5. Kim J H, Oh S, Heo Y-U, Hata S, Kumakura H, Matsumoto A, Choi S, Shimada, Maeda Y M, MacManus-Driscoll J L and Dou S X, 2012 NPG Asia Materials, 4 doi:10.1038/am.2012.3.
6. Muralidhar M, Inoue K, Koblishka MR, Tomita M and Murakami M 2014 J. Alloys Compd. 608 102.
7. Fuchs G, Müller K-H, Handstein A, Nenkov K, Narozhnyi V.N, Eckert D, Wolf M and Schultz L 2011 Solid State Communications 118 497.
8. Muralidhar M, Nozaki K, Kobayashi H, Zeng X L, Koblishka-Veneva A, Koblishka MR, Inoue K and Murakami M 2015 J. Alloys Compd. 649 833.
9. Anurag Gupta and A V Narlikar 2009 Supercond. Sci. Technol. 22 125029.
10. Muralidhar M, Higuchi M, Jirsa M, Diko P, Kobal I and Murakami M 2017 IEEE Transactions of Applied Superconductivity, 27 6201104.
11. Longji Dadiel J, Muralidhar M and Murakami M 2018 J. Phys. Conf. Ser. 1054 012052.
12. Chen D and Goldfarb R B 1989 J. Appl. Phys. 66 2489.
13. Muralidhar M, Kenta N, Koblishka MR and Murakami M 2015 Physica Status Solidi a, 212 2141.
14. Lee S, Masui T, Yamamoto A, Uchiyama H and Tajima S 2003 Physica C 397 7.
15. Yamamoto A, Shimoyama J, Ueda S, Iwayama I, Horii S, Kishio K 2005 Supercond. Sci. Technol. 18 1323.
16. Avdeeva M, Jorgensen J D, Ribeiro R A, BudÕkob S L and Canfield P C 2003 Physica C 387 301.
17. Wilke R H T, Bud’ko S L, Canfield P C and Finnemore D K, 2004 Phys. Rev. Lett. 92 217003.
18. Muralidhar M, Higuchi M, Diko P, Jirsa M and Murakami M 2017 J. Phys. Conf. Ser. 871 012056.
19. Hampshire D P and Jones H 1987 J. Phys. C 21 419.