Production and Characterization of Bulk MgB$_2$ Material made by the Combination of Crystalline and Carbon Coated Amorphous Boron Powders

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Abstract. The object of this investigation is to reduce the cost of bulk production and in the same time to increase the critical current performance of bulk MgB$_2$ material. High-purity commercial powders of Mg metal (99.9% purity) and two types of crystalline (99% purity) and 16.5 wt% carbon-coated, nanometer-sized amorphous boron powders (98.5% purity) were mixed in a nominal composition of MgB$_2$ to reduce the boron cost and to see the effect on the superconducting and magnetic properties. Several samples were produced mixing the crystalline boron and carbon-coated, nanometer-sized amorphous boron powders in varying ratios (50:50, 60:40, 70:30, 80:20, 90:10) and synthesized using a single-step process using the solid state reaction around 800 °C for 3 h in pure argon atmosphere. The magnetization measurements exhibited a sharp superconducting transition temperature with $T_{\text{onset}}$ around 38.6 K to 37.2 K for the bulk samples prepared utilizing the mixture of crystalline boron and 16.5% carbon-coated amorphous boron. The critical current density at higher magnetic field was improved with addition of carbon-coated boron to crystalline boron in a ratio of 80:20. The highest self-field $J_c$ around 215,000 A/cm$^2$ and 37,000 A/cm$^2$ were recorded at 20 K, self-field and 2 T for the sample with a ratio of 80:10. The present results clearly demonstrate that the bulk MgB$_2$ performance can be improved by adding carbon-coated nano boron to crystalline boron, which will be attractive to reduce the cost of bulk MgB$_2$ material for several industrial applications.

1. Introduction
Since 2001, the discovery of superconductivity in MgB$_2$ material has led to notable progress concerning especially the understanding of the origin of the large $T_c$, processing, characterization, and industrial applications [1-3]. The intermetallic material is more attractive for the next generation of superconducting applications because of the lack of weak-links at the grain boundaries and a high critical transition temperature of 39 K as compared to the conventional NbTi. The superconducting transition temperature of MgB$_2$ is significantly lower than that of YBa$_2$Cu$_3$O$_y$ “Y-123”, instead, MgB$_2$ benefits of a high critical current density ($J_c$) in the polycrystalline state, which makes these materials promising candidates for several industrial applications including the next generation of super-magnets for medical devices, electrical power system, transportation and powerful super-magnets operating at around 20 K [3-9]. For superconducting super-magnet applications, it is required to produce good quality, low cost MgB$_2$ material with high $J_c$ and an acceptable mechanical performance. To improve the critical current density of the MgB$_2$ material, a variety of processing techniques have been developed and studied in
terms of commercially usefulness [9,10]. On the other hand, to improve the critical current density of these materials a variety of dopants [11-14] were adopted and very successful results were observed, especially using carbon-based dopants, e.g., carbon, boron carbide, carbon nanotubes, carbohydrates or hydrocarbons, graphene oxide, carbon-coated boron powders, etc. [15-19]. As a result, several researchers observed a dramatic improvement of the superconducting properties such as the irreversibility field, \( H_{irr} \), the upper critical field, \( H_{c2} \), or the critical current density, \( J_c \), under high magnetic fields. Further, significant improvements in self-field performance were reached by optimizing the microstructure [10]. Our recent results also clarified that atomic force microscopy and EBSD observations clearly indicated that the observed grains exhibit grain sizes in the nanometer range and their density was high in the samples sintered for 3 h at 800 °C and 805 °C. Further, the samples sintered at 805 °C for 3 h showed a high critical current density of 245 kA/cm\(^2\) at 20 K [10]. Moreover, the samples sintered at 775 °C for 1 h showed a high critical current density of 270 kA/cm\(^2\) at 20 K [20].

The latest reports also suggested that the bulk MgB\(_2\) materials’ performance can be further improved by tuning both the optimum sintering temperature and the optimal sintering time. To utilize the bulk MgB\(_2\) material for several industrial applications, one needs batch production, cheaper processing, and a high performance. In the present work, we study the effect of mixture of crystalline and 16.5 wt% carbon-coated, nanometer-sized amorphous boron powders were mixed in a nominal composition of MgB\(_2\) to reduce the boron cost and studied the X-ray diffraction and superconducting performance especially the \( T_c \) and \( J_c \).

2. Experimental details

The bulk polycrystalline MgB\(_2\) samples were fabricated by using in-situ solid state reaction. High-purity commercial powders (Furu-uchi Chemical Corporation, Japan) of Mg metal (99.9% purity, 325 meshes) and 16.5 wt% carbon-encapsulated amorphous nano-boron powders (85% purity) were mixed in a nominal ratio of Mg: B = 1:2. For any industrial applications, low cost raw materials are crucial to reduce the products final costs. Amorphous boron powders always yield high performance as compared to the crystalline boron powders. However, the cost of the amorphous or carbon coated amorphous boron powders is three to four times higher as compared to the crystalline boron powders. Therefore, to reduce the cost of the boron and to optimize the high critical current density, several samples were produced mixing the crystalline boron and the 16.5% carbon-coated, nanometer-sized amorphous boron powders in varying ratios, i.e., 50:50, 60:40, 70:30, 80:20, 90:10. More details for the 16.5 wt% carbon-encapsulated nano-boron powders (provided by PAVEZYUM, Advanced Chemicals, Turkey) can be found elsewhere [21]. The powder mixture was pressed into pellets of 20 mm in diameter and 4 mm in thickness using an uniaxial pressing machine. The consolidated pellets were then wrapped in tantalum foils and subjected to the heat treatment in Ar atmosphere in a tube furnace. The samples were heated to the target sintering temperature of 800 °C and kept there for 3 h in flowing argon gas. Finally, the temperature was lowered to room temperature at a cooling rate of 100 °C/h.

The constituent phases of the samples were identified with a high-resolution automated X-ray powder diffractometer (RINT2200), using Cu-K\(_x\) radiation generated at 40 kV and 40 mA. Small specimens with dimensions of 1.5 × 1.5 × 0.5 mm\(^3\) were cut from bulk MgB\(_2\) samples and subjected to the measurements of the critical temperature (\( T_c \)) and magnetization hysteresis loops (\( M-H \) loops) in applied magnetic fields from −1 to +5 T at temperatures of 20 K using a SQUID magnetometer (Quantum Design, model MPMS5). The magnetic \( J_c \) values were estimated based on the extended Bean critical state model using the relation

\[
J_c = \frac{20 \Delta m (a^2/3)}{d} \quad (1)
\]

where \( d \) is the sample thickness, \( a, b \) are cross sectional dimensions, \( b \geq a \), and \( \Delta m \) is the difference of magnetic moments during increasing and decreasing field in the \( M-H \) loop [22].
3. Results and discussion

X-ray diffraction patterns observed on the bulk MgB$_2$ produced using the mixture of the crystalline boron and 16.5% carbon-coated, nanometer-sized amorphous boron powders in varying ratios i.e. 50:50, 60:40, 70:30, 80:20, 90:10 are presented in Fig. 1. From the figure it is clear that the main phase was MgB$_2$ for all the samples, which is similar to the earlier reports [9]. There was a very small trace of MgO. Thus it is in agreement with the fact that oxygen could trap the material during sample pressing into pellets or wrapping into tantalum foils before loading the furnace [20]. The magnified view of the region around 56 degrees, which shows the peaks (0 0 2) and (1 1 0) in detail (see Fig.1, right). From the figure it is clear that the (1 1 0) peak for the 16.5% carbon-encapsulated Boron added samples is slightly shifted to higher angles as compared to the sample produced using the crystalline boron. The (0 0 2) peak position stood unchanged for all samples studied. It indicates that carbon partly substitutes for boron in the lattice of MgB$_2$, which is similar to earlier reports [14,21].

![Figure 1. X-ray diffraction patterns of bulk MgB$_2$ samples produced using the mixture of the crystalline boron and 16.5% carbon-coated, nanometer-sized amorphous boron powders in varying ratios (50:50, 60:40, 70:30, 80:20, 90:10) and sintered at 800 °C for 3h in argon atmosphere (left); the enlarged view of (0 0 2) and (1 1 0) peaks for the same material (right).](image-url)

Figure 2 shows temperature dependence of magnetic susceptibility curves of MgB$_2$ samples produced using the mixture of the crystalline boron and 16.5% carbon-coated, nanometer-sized amorphous boron powders in varying ratios i.e. 50:50, 60:40, 70:30, 80:20, 90:10 in a magnetic field of 1 mT. It is evident that superconducting transition temperature ($T_c$) is decreased with increasing the 16.5% carbon-coated, nanometer-sized amorphous boron in the crystalline boron (see Table 1). The high $T_c$ of 38.65 K was observed for sample produced utilizing the crystalline boron. On the other hand, MgB$_2$ sample produced mixture of the crystalline boron and 16.5% carbon-coated, nanometer-sized amorphous boron powders, i.e., 50:50 is 32.99 K. The good $T_c$ indicate that all processed bulk MgB$_2$ samples were good in quality (see Table 1).

The observed superconducting transition temperatures are similar to recently reported bulk MgB$_2$ material fabricated with a sintering process [19]. These results suggest that superconducting transition temperature are not effected much when we add the carbon-coated, nanometer-sized amorphous boron powders in crystalline boron.

In order to evaluative the critical current performance of the MgB$_2$ material produced by the mixture of the crystalline boron and 16.5% carbon-coated, nanometer-sized amorphous boron powders, we measured the magnetization hysteresis loop ($M$-$H$ loop) in fields from $-1$ to $+5$ T at 20 K using a SQUID magnetometer (Quantum Design, model MPMS5) and the critical current density ($J_c$) was estimated using Bean’s critical state formula and it was presented in Figure 3.
Table 1. Superconducting transitions temperatures and critical current density at 20K for MgB$_2$ materials

| Boron content in MgB$_2$ | $T_c$ (K) | $J_c$ at 20 K (A/cm$^2$) |
|--------------------------|-----------|------------------------|
| CB 100%                  | 38.66     | 211083                 |
| CB 90%+CCB 10%           | 38.10     | 214755                 |
| CB 80%+CCB 20%           | 36.80     | 197490                 |
| CB 70%+CCB 30%           | 35.76     | 152899                 |
| CB 60%+CCB 40%           | 34.99     | 73880                  |
| CB 50%+CCB 50%           | 32.99     | 25151                  |

Figure 2. Superconducting transition in the bulk MgB$_2$ materials produced using the mixture of the crystalline boron and 16.5% carbon-coated, nanometer-sized amorphous boron powders and sintered at 800 °C for 3 h in argon atmosphere and measured in a magnetic field of 1 mT.

Figure 3. Field dependence of the critical current densities ($T = 20$ K) for MgB$_2$ superconductor produced using the mixture of the crystalline boron and 16.5% carbon-coated, nanometer-sized amorphous boron powders and sintered at 800 °C for 3 h in argon atmosphere.
It was notable that critical current density was increased especially at higher magnetic field the samples produced utilizing the mixture of 16.5% carbon-coated, nanometer-sized amorphous boron powders (see Fig. 3). Further, the highest self-field \( J_c \) was recorded to be 215,000 A/cm² at 20 K in MgB\(_2\) samples produced mixture of crystalline boron and the carbon-coated amorphous boron powders ratio is 90:10. These values are still high as compared to samples produced from 100% amorphous boron powders [20]. The summary of the \( J_c \) performance for all produced samples is given in Table 1. It is clear that high field critical current performance was more than double in samples the carbon-coated amorphous boron powders ratio is 10:90 and 20:80 as compared to samples made by crystalline boron powders. Further, it is important to note that the irreversibility field was improved with increasing the carbon-coated amorphous boron and crystalline boron powders ratio from 10:90, 20:80, and 30:70; higher ratios lead to a decrease of the irreversibility fields. The carbon-coated amorphous boron and crystalline boron powders ratio of 80:20 exhibited the highest irreversibility among all the samples. It has been reported by several authors that carbon substituted at boron sites is effective in improving the critical current performance, especially at high magnetic fields and decreases the superconducting transition temperature. Further, it was also clarified in bulks and tapes that carbon doping introduced defects into the sample, which can act as strong pinning centers, leading to the improved performance at higher fields, and as a result, to an improvement in irreversibility. Moreover, the present results indicate that the 16.5 wt% carbon-coated amorphous boron powders addition to the crystalline boron is crucial to improve the quality of bulk MgB\(_2\) materials made by crystalline boron powders, which will be defiantly reduce the prize of the MgB\(_2\) simples and eventually improve the high field performance for the industrial applications.

4. Conclusions
Several bulk MgB\(_2\) samples were produced mixing the crystalline boron and carbon-coated, nanometer-sized amorphous boron and synthesized using a single-step process using the solid state reaction at 800 °C for 3 h in pure argon atmosphere. X-ray diffraction results indicated that all samples are single phase MgB\(_2\) along with small quantity of MgO. DC susceptibility vs. temperature measurements showed a sharp superconducting transition around 38 K. The bulk MgB\(_2\) samples made by crystalline and carbon-coated, amorphous boron ratio 90:10 and 80:20 exhibited enhanced \( J_c \) value at 2 to 4 T at 20K. These results imply that high flux pinning performance of the sintered bulk MgB\(_2\) material can be produced using the small quantity of 16.5 wt% carbon-coated boron powders addition to the crystalline boron powders, which will be very useful to reduce the boron cost by means of production of cheap superconducting super-magnets.

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