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Production and Characterization of Bulk MgB_2 Material made by the Combination of Crystalline and Carbon Coated Amorphous Boron Powders

K. Hiroki[1], M. Muralidhar[1*], M.R. Koblischka[2], M. Murakami[1]

[1] Superconducting Material Laboratory, Graduate School of Science and Engineering, Shibaura Institute of Technology, 3-7-5 Toyosu, Koto-ku, Tokyo 135-8546, Japan
[2]Institure of Experimental Physics, Saarland University, P.O. Box 151150, 66041Saarbrucken, Germany

[*]miryala1@shibaura-it.ac.jp

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 $T_{c,onset}$ 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 $YBa_2Cu_3O_y$ "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_α 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

$$J_c = 20\,\Delta m/[a^2 d\,(b-a/3)] \quad , \qquad (1)$$

where d is the sample thickness, a, b are cross sectional dimensions, $b \geq a$, and Δm 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 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].

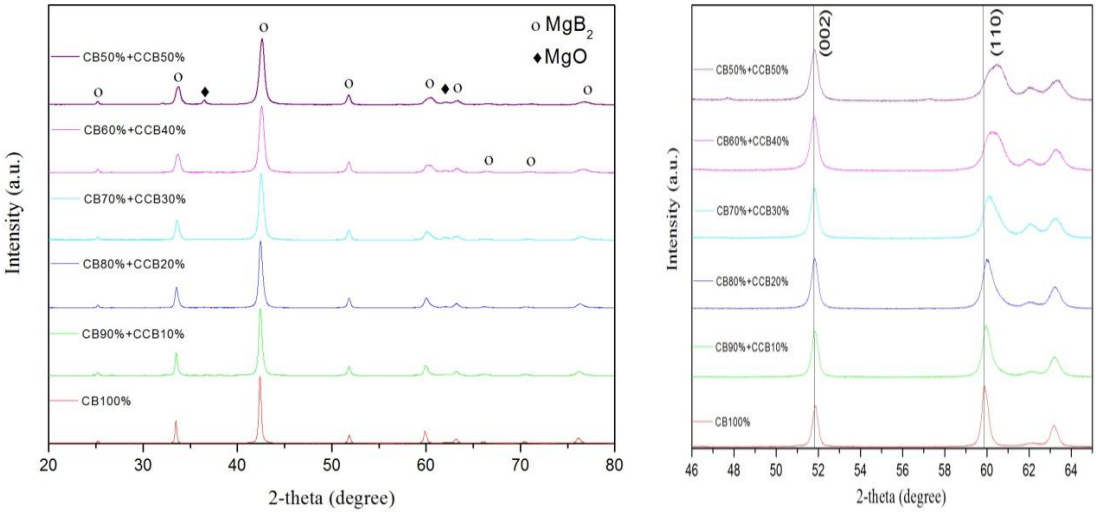

Figure 1. X-ray diffraction patterns of bulk MgB_2 samples produced using the mixture of the crystalline boron and 16.5% carbon-coated, nanometer-sized amorphous boron powders in varying ratios (50:50, 60:40, 70:30, 80:20, 90:10) and sintered at 800 ^{o}C for 3h in argon atmosphere (left); the enlarged view of (0 0 2) and (1 1 0) peaks for the same material (right).

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 ($T_{c,onset}$) 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.

Table1. 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)			
		Self-field	2 T	3 T	4 T
CB 100%	38.66	211083	24813	4386	158
CB 90%+CCB 10%	38.10	214755	37029	10413	1997
CB 80%+CCB 20%	36.80	197490	33399	11638	2947
CB 70%+CCB 30%	35.76	152899	17894	6291	851
CB 60%+CCB 40%	34.99	73880	5245	1410	11
CB 50%+CCB 50%	32.99	25151	621	41	

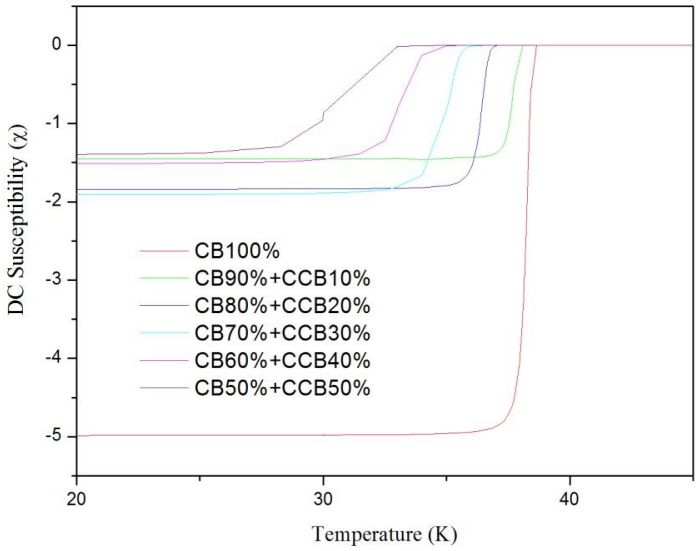

Figure 2. Superconducting transition in the bulk MgB_2 materials produced using the mixture of the crystalline boron and 16.5% carbon-coated, nanometer-sized amorphous boron powders and sintered at 800 ºC for 3 h in argon atmosphere and measured in a magnetic field of 1 mT.

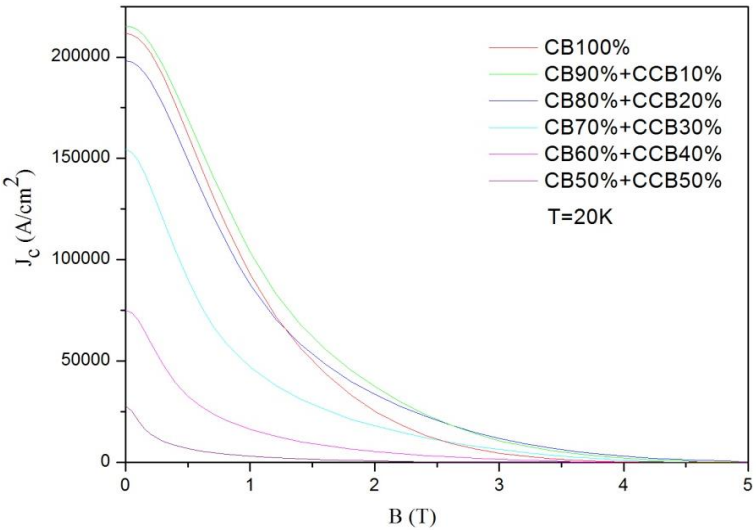

Figure 3. Field dependence of the critical current densities (T = 20 K) for MgB_2 superconductor produced using the mixture of the crystalline boron and 16.5% carbon-coated, nanometer-sized amorphous boron powders and sintered at 800 ºC for 3 h in argon atmosphere.

It was notable that critical current density was increased especially at higher magmatic 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/cm^2 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 4T 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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