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Superconducting Properties of MgB_2 Wire Using Ball-Milled Low Purity Boron

Xun Xu, Jung Ho Kim, Yun Zhang, Yue Zhao, Matthew Rindfleisch, and Michael Tomsic

***Abstract*—MgB_2/Fe wire samples were prepared by using ball-milled 96% boron (B) powder with strong semi-crystalline phase. We observed samples that contained ball-milled 96% B in comparison with one made from as-supplied commercial 96% B, with the results showing a significant enhancement in the high field transport critical current density (J_{ct}) due to small grain size and better reactivity. However, the inter-grain connectivity became worse, which could lead to poor J_{ct} in low field and an increased level of disorder.**

***Index Terms*—Ball milling, magnetic critical current density, MgB_2 wire, oxygen.**

I. Introduction

ENORMOUS research efforts have been directed at MgB_2 in the past seven years since its discovery in 2001 [1], focusing on materials performance properties, wire conductor development, and coil demonstrations. Unfortunately, however, the critical current density (J_c) of un-doped MgB_2 is drastically decreased with an increasing external field. This is because of its poor flux pinning properties, when compared to high temperature superconductors (HTS) [2].

In polycrystalline wire and tape samples, significant breakthroughs in the improvement of critical current density (J_c), irreversibility field (B_{irr}), and upper critical field (B_{c2}) were achieved through chemical doping. Such doping is effective in improving the J_c B characteristics of MgB_2, especially in the high field region. However, the connectivity between the grains might be further improved.

In un-doped polycrystalline MgB_2 samples, however, grain boundary pinning seems to play the dominant role. So, the precursor powders are very important for the properties of the final material. MgB_2 grain size is strongly influenced by the particle size of the precursor powders, especially of the boron (B) powder [3]–[6]. Mechanical alloying of the precursor powders reduces the grain size and improves the critical current [7]–[9].

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Our group focused on the phase transformation and superconducting properties of MgB_2 bulk samples created from ball-milled boron (B) powder. As the first step, we studied the effects of ball milling, using different media such as acetone, ethanol, and toluene, on the microstructures and J_c of the resulting MgB_2 samples. Using toluene processing led to enhancements in the magnetic critical current density (J_{cm}) in high field [10]. Recently, it has been shown that the reactivity of low-cost 96% B powder can be improved by using ball-mill processing, leading to enhanced magnetic critical current density compared to the original 96% B powder [11]. However, these bulk sample results just raised the possibility of using low grade 96% B powder, since the performance of MgB_2/Fe wire made from ball-milled low purity boron is much more important for industrial applications.

In this work, we evaluated the superconducting properties of MgB_2/Fe made from low-grade 96% commercial B powder with a strong semi-crystalline phase. The particle size of B, the transport critical current density (J_{ct}), and the microstructures of MgB_2 wire using the ball-milled B are presented in comparison with a reference sample made under the same sintering conditions.

II. Experimental Methods

MgB_2/Fe monofilament wires were prepared by an *in situ* reaction process and the powder-in-tube method. B powder (Tangshan WeiHao, China) with strong semi-crystalline phase (Boron 96%, Magnesium 1.79%, H_2O_2 Insoluble 0.93%, Moisture 0.17%, etc.) was processed by ball milling, with toluene as the ball-milling medium. The ball-milling process was carried out for 12 hrs at a rotation speed of 160 rpm. The powder to ball ratio was 1: 16 in a planetary ball-mill with an agate jar and balls 5 mm and 10 mm in size. The powders were then dried in a vacuum oven to evaporate the toluene. For our experiments, two kinds of B powders were prepared, with and without ball milling: these are denoted by BP96 and P96, respectively. Here, the ball-milled boron is denoted by the initial B. The boron powder particle size and distribution were determined by a JL-1166 Laser Particle Sizer. We also prepared a reference MgB_2 sample using 99% amorphous B for comparison.

Magnesium (99%, 325 mesh) and the different boron powders with the nominal atomic ratio of $Mg: B = 1 : 2$ to ball-milled boron were mixed through grinding and were put into Fe tubes with a length of 140 mm, an outer diameter (O.D) of 10 mm, and an inner diameter (I.D) of 8 mm. The packing process was car- ried out in air. Both ends of the tubes were sealed with aluminum pieces, and then the tubes were drawn to a wire with a diameter

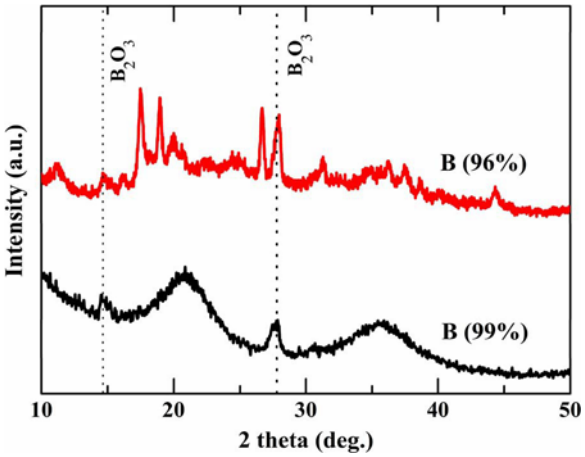

Fig. 1. XRD patterns for different boron powders.

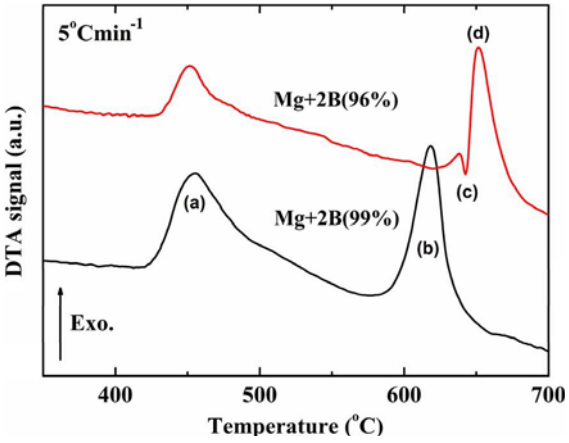

Fig. 2. Differential thermal analysis for MgB_2 with different boron powders.

of 1.4 mm. Short wire samples (4 cm each) were sealed with Zr foil, then sintered, with a heating rate of $5°C\ min^{-1}$ in flowing high purity Ar to 700°C and a dwell time at the final temperature of 30 minutes, followed by furnace cooling to room temperature. The volume fraction of the superconducting core in the final wire was approximately 48%. The transport critical current (I_c) at 4.2 K was measured by the standard DC four-probe resistive method with a criterion of $1\ \mu Vcm^{-1}$ in magnetic fields up to 12 T. The magnetization was measured at 5 and 20 K using a Physical Properties Measurement System (PPMS, Quantum Design) in a time-varying magnetic field with a 50 $Oe \cdot s^{-1}$ sweep rate up to 8.5 T. All the samples had their iron sheaths peeled off for measurements and were rod-shaped with a length of 2.5 mm. The magnetic J_c was derived from the width of the magnetization loop using Bean's model [12]. The grain morphology and the microstructure of the MgB_2 with ball-milled boron and without ball-milled boron were studied by scanning electron microscopy (SEM).

III. Results and Discussion

A. Boron Powder With Different Purities

Fig. 1 shows the x-ray diffraction (XRD) patterns for the 96% semi-crystalline boron and 99% amorphous boron powders. The patterns can be indexed according to single phase boron, except for the B_2O_3 peaks ($2\theta \approx 14.6°$ and 27.8°), which are indicated with dashed lines for both powders.

Furthermore, to examine the phase transformation of MgB_2 using 99% B and 96% B, differential thermal analysis (DTA) was performed, and the results are shown in Fig. 2. The heating rate was $5°C\ min^{-1}$ under flowing Ar, as with our sintering conditions. In both samples, there were two exothermal peaks: The first exothermal peak (a) is due to the reaction between melted B_2O_3 and Mg. The B_2O_3 has no melting point, but rather a progressive softening and melting range from 300°C to 700°C under particular conditions [11]. The crystals begin to break down at 300°C, and a series of sub-oxides are produced with partial melting until full fusion is reached at 700°C. The main reason for the presence of B_2O_3 in the B powder is because B has partially oxidized in air. As for the second exothermal peak (b), it can be attributed to the MgB_2 phase formation. What is interesting is that the second exothermal peaks of the two samples, (b) and (d), show different behavior. Specifically, the second exothermal peak of the sample using 96% B was slightly shifted to higher temperature, unlike the sample using 99% B. In addition, there was a weak endothermal peak (c) before the exothermal peak related to MgB_2 phase formation (d). This weak peak is related to the melting of Mg at around 650°C. Using 96% B with crystalline phase can introduce shifting of the second exothermal peak. We conclude that phase formation of MgB_2 using 96% B with some crystalline B can occur after the Mg has melted. This is because using B with crystalline phase requires more energy, due to poor reactivity between Mg and B [3]. This information was of importance in determining optimal sintering conditions for our samples. We speculate that the appropriate sintering temperature is above 650°C for MgB_2 using 96% B, and in particular, above the Mg melting point. Note that the first exothermal peak did not shift to higher temperature. If this peak were related to the solid-solid reaction of MgB_2, this would also be shifted because of the different crystallinity.

B. Selected Media for Ball-Milling

For this reason, we tried to modify the semi-crystalline boron *via* wet milling. As a first step, we studied the effects of different ball-milling media, such as acetone (C_3H_6O), ethanol (C_2H_6O), and toluene (C_7H_8), because these liquid media help to make mixing homogeneous. Fig. 3 shows the magnetic field dependence of J_c for all samples at 5 and 20 K, including J_c of the reference sample made from as-supplied 99% B. The J_c value of the toluene sample was estimated to be $5 \times 10^3\ Acm^{-2}$ at 8 T and 5 K. This value is comparable to those of chemically doped samples under high field. The J_c value is much higher than that of the pure reference MgB_2 made without any ball-milling process, by a factor of 20. Using ball-milled B with toluene as the ball-milling medium was a highly effective method to enhance the $J_c(B)$ performance under high field. This is because toluene can prevent the oxidation of B powder during ball milling, and the small grain size is effective for enhancing flux pinning at the grain boundaries, which represent effective pinning centers. However, at 20 K, the $J_c(B)$ performance of the toluene sample is slightly lower than

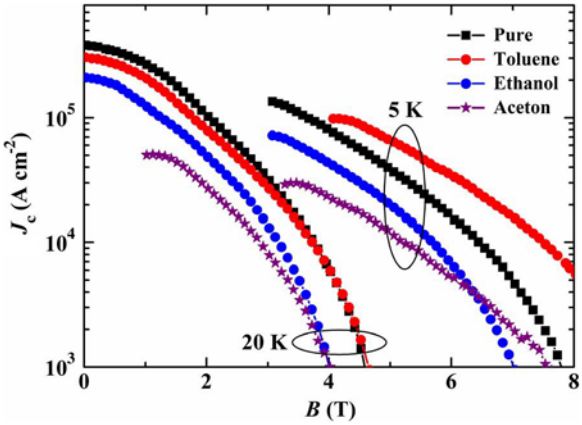

Fig. 3. The magnetic critical current density (J_{cm}) as a function of field for the MgB_2 samples [10].

TABLE I
PARTICLE SIZE DISTRIBUTION FOR BORON POWDERS

	P96	BP96
D10 (μm)	0.23	0.13
D50 (μm)	0.84	0.24
D90 (μm)	2.40	0.48

that of the reference MgB_2 sample. This is probably because the ball-milled sample had poor grain connectivity.

C. MgB_2 Wire Results With the Ball-Milled 96% Boron

Table I shows the particle size distributions of (a) P96 and (b) BP96. It can be clearly seen that after 12 hrs ball-milling, the original P96 powder size range changed from 0–3 to 0–0.75 μm. The median value (D50) is termed the average particle diameter. This median particle size was reduced from 0.84 μm to 0.24 μm. At the same time, if effects from the shape of the B powder are neglected, the small particles led to a more than twofold increase in the specific surface area value, which should improve the reactivity of BP96 powder under the same solid reaction conditions as the original P96. On the other hand, during the formation of MgB_2, if the same particle size of Mg powder and fixed sintering conditions are used, the MgB_2 particle size is determined by the particle size of the B powder. So, the MgB_2 that is formed from ball-milled B powder (BP96) should have small grain size, which must improve the superconducting properties of the sample.

SEM images of MgB_2 wires made from (a) as-supplied boron (P96) and (b) ball-milled boron powders (BP96), denoted as WPS700 and WBPS700, respectively, are shown in Fig. 4. Here, it is clearly observed that the average grain size of the sample prepared from the ball-milled boron is much smaller than in the sample made from the as-supplied boron. The ball-milled sample also seems to be more consolidated.

The transport current $J_{ct} - B$ performance of these two samples is shown in Fig. 5. It can be clearly seen that the J_{ct} of samples prepared from the ball-milled boron showed better performance in the field range of 5 to 12 T. This indicates that ball

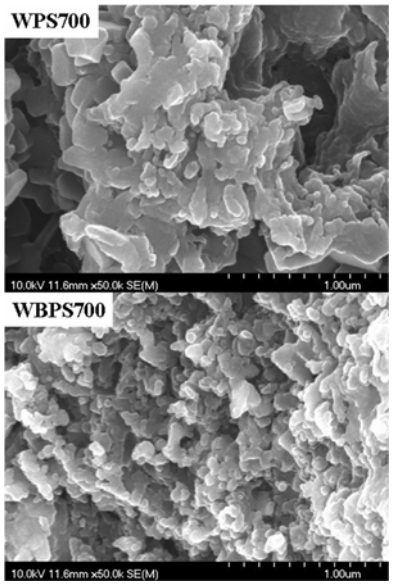

Fig. 4. Scanning electron microscope (SEM) images for (top) wire sample prepared from as-supplied boron, and (bottom) wire sample prepared from ball-milled boron. All samples were sintered at 700 °C for 30 minutes.

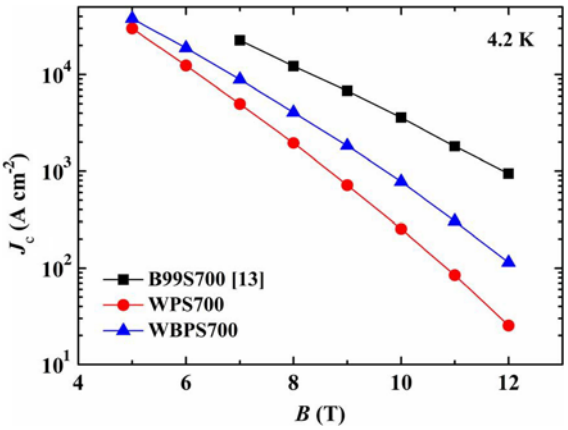

Fig. 5. Transport critical current density (J_{ct}) for MgB_2 wires as a function of external magnetic field at 4.2 K B99S700 is the reference sample from 99% B.

milling causes reduction of the MgB_2 grain size, which could act as a source of strong pinning centers due to the increased number of grain boundaries, as mentioned above. However it was concluded that the ball-milling could not help to improve the J_{ct} at magnetic fields below 5 T. Compared to the magnetic J_{cm} under magnetic fields of 5 to 8 T, the transport J_{ct} advantage is lower. Note that the transport current capacity is the real useful J_c that flows through the whole of the sample. That is to say, the differences between J_{cm} and J_{ct} in MgB_2 may be related to features of the microstructure of the superconducting MgB_2 core, such as porosity, agglomeration of superconducting crystals, and fraction of MgO as the main secondary phase. These could have negative effects on the J_{ct}, by acting as obstacles to current flow. Quite interestingly, the effects of these obstacles do not appear in magnetic loop measurements. That is why the magnetic J_{cm} does not represent the real J_c of MgB_2 wires [14].

IV. Conclusion

In summary, a study of ball-milling effects on the transport critical current density (J_{ct}) of MgB_2/Fe wires has been conducted. We observed that lattice disorder increased due to the ball milling. It caused both a slight reduction in the transition temperature and degradation of connectivity. It is the main cause for the enhancement of the critical current in the high field region.

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