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Improved J_c of MgB_2 superconductor by ball milling using different media

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Abstract

In this paper, the effects of ball milling B powders using different media, such as acetone, ethanol, and toluene on the superconducting properties of MgB_2 have been studied. It was observed that toluene medium was the most effective of them all for enhancing J_c. J_c was estimated to be 5 x 10^3 A/cm^2 at 8 T and 5 K. This value is much higher than that of pure MgB_2 that was not ball milled, by a factor of 20. It was considered that ball-milled B using toluene leads to smaller MgB_2 grains, resulting in enhanced J_c at low operating temperature and high field.

(Some figures in this article are in color only in the electronic version)

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1. Introduction

The discovery of the superconductivity of MgB_2 with a critical temperature of 39 K has offered the promise of important large-scale and electronic device applications at around 20 K [1]. A significant enhancement in the J_c of MgB_2 has been achieved through chemical doping with carbon (C) containing compounds, such SiC, C, B_4C, and CNT. However, doping effects have been limited by the agglomeration of nanosized dopants and poor reactivity between boron (B) and C [2-7]. Moreover, the self-field and low-field J_c were depressed due to the decrease in the superconducting volume. To improve these properties, various methods have been reported. They include, for example, a ball-milling method [8,9], a thermo-mechanical processing method [10], and the use of MgH_2 powder instead of Mg [11]. Among them, the ball-milling method is particularly interesting, as size control of the starting material may induce more effective pinning without any dopants. Specifically, the properties of the B powder, such as purity and size, may play an important role in determining the final properties of the MgB_2 [12]. This is because melting Mg can be diffused into B powder to form MgB_2 phases during sintering.

Fischer et al. fabricated MgB_2 wires and bulks by a mechanical alloying method [10]. They obtained one of the highest J_c values without any other elements added. The very fine-grained nanocrystalline microstructure of the superconducting phase seems to be responsible for the excellent J_c values (1×10^5 A/cm^2 at 2.1 T and 20 K). Fang et al. fabricated MgB_2/Fe tapes via the powder-in-tube method using an ultra-fine Mg and B precursor mixture prepared by high energy ball milling. The J_c was estimated to be 2.0×10^5 A/cm^2 at 20 K and 0.6 T, and 1.1×10^5A/cm^2 at 1.5 T [8]. Kondo et al. reported that the magnetic J_c of MgB_2 depended on the different insert gases, Ar and H_2, that were used during ball milling [9]. However, there was no systematic study of the effects of different ball-milling media, such as acetone (C_3H_6O), ethanol (C_2H_6O), and toluene (C_7H_8). It is these liquid media that help to make mixing homogeneous. On the other hand, these media consist of carbon (C), oxygen (O), and hydrogen (H), so that the O can easily react with Mg and B to form MgO and B_2O_3 during the drying process after ball milling. In our

study, therefore, we evaluated the effects of ball-milled B powders that were produced using different media, such as acetone, ethanol, and toluene, on the superconducting properties of MgB_2. The lattice parameters, J_c, T_c, and microstructure are presented in comparison with reference pure MgB_2.

2. Experiment details

MgB_2 pellets were prepared by an *in-situ* reaction process. B powders (99%) were prepared in different ball-milling media, such as acetone, ethanol, and toluene (with the samples named after the corresponding medium). The ball-milling process was carried out for 4 hr with a rotating speed of 160 rpm under air. These three kinds of B powders were mixed, ground, and pressed with Mg (99%) powder. All samples were sintered at 650^{o}C for 30 min under high purity argon gas. The heating rate was 5^{o}C/min. A pure reference MgB2 sample (referred to as pure) was also fabricated for comparison by applying the same process, except for the ball milling. All samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The crystal structure was refined with the aid of the program FullProf. T_c was defined as the onset temperature at which diamagnetic properties were observed. The magnetization was measured at 5 and 20 K using a Physical Property Measurement System (PPMS, Quantum Design) in a time-varying magnetic field with sweep rate 50 Oe/s and amplitude 8.5 T. Since there is a large sample size effect on the magnetic J_c for MgB_2, all the samples for measurement were made to the same size (1 x 2 x 3 mm^3) for comparison. The magnetic J_c was derived from the width of the magnetization loop using Bean's model [13]. J_c versus magnetic field was measured up to 8.5 T.

3. Results and discussion

Table 1 shows the data measured for the pure reference MgB_2 and the ball milled MgB_2 samples using different media. The *a* and *c* lattice constants for all samples did not change within the limit of calculation error, suggesting that C could not substitute into B sites during ball milling. Even

though the hydrocarbon media used contained C, there were no apparent substitution effects. However, it is to be noted that T_c for all ball-milled samples was a little decreased. In addition, the *a* lattice parameter for the toluene sample is shorter than that of the other ball-milled samples. This is probably because the toluene sample has a low T_c value. This low T_c value might be one of the possible reasons for the low crystallinity of ball milling sample. These observations were further explained by the FWHM values and refined grain sizes, to be discussed later.

The XRD patterns for all samples are shown in Figure 1. The XRD measurements were performed on the ground MgB_2 pellets. It was observed that all samples seemed to be well developed MgB_2 with small amounts of MgO. There were no visible differences in this respect between the samples. From the XRD results, the FWHMs of the (100), (002), and (110) peaks were evaluated as listed in Table 1. It is to be noted that the FWHMs of the 3 main peak positions for the toluene sample were much larger. This significant broadening of the (002) and (110) peaks can be explained by depression of crystallinity due to ball milling. According to the Scherrer equation, an increased FWHM value also indicates that the grain size has decreased as follows:

$$D_p = 0.94\lambda / \beta_{1/2} \cos\theta$$

where D_p is crystal size, λ is wavelength, $\beta_{1/2}$ is FWHM, and θ is peak position. From this equation, crystal size is easily calculated as a function of peak width (FWHM). This approach does, however, neglect the effect that strain can have on crystallite size [14]. As a result, broadening FWHM values may be due to ball milling with different media. Yamada *et al.* reported that a small MgB_2 grain size was effective in enhancing flux pinning because the grain boundaries of MgB_2 represented effective pinning centers, as in the case of A15 metallic superconductors [15].

Figure 2 shows SEM images for all samples sintered at 650^{o}C for 30 min. It was observed that the specimens consisted of quite well consolidated material. The grain size of the material is quite small, around 100-300 nm. Specifically, the grain sizes of the ethanol and acetone samples are

larger than for the pure reference sample (~200 nm), while the grain size of the toluene sample was slightly smaller (~100 nm). It is to be noted that the reference sample has better grain homogeneity, but the toluene sample seems to have enhanced clumping of fine particles into coral-like agglomerates due to ball-milling effects. The different behaviours of $J_c(B)$ and T_c can be attributed to this microstructural difference. Since melting Mg is diffused into B powder to form MgB_2 phases during sintering, $J_c(B)$ properties can be related to the B powder properties.

Figure 3 shows the magnetic field dependence of J_c for all samples at 5 and 20 K. We observe that the J_c value of toluene sample was estimated to be 5 x 10^3A/cm^2 at 8T and 5K. 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 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 20K, the $J_c(B)$ performance of the toluene sample value is slightly lower than that of the reference MgB_2 sample. This is probably because the ball-milled sample had poor grain connectivity. This observation is further supported by the FWHM and SEM results (Table 1 and Figure 2).

The critical temperature (T_c) for all samples is presented in Figure 4. T_c of the reference MgB_2 was higher than that of the ball-milled samples. This is related to the improvement of crystallinity of the MgB_2 superconductor. It is to be noted that the T_c variations of the ball-milled samples are significantly different for the different media. In addition, T_c of the toluene sample was slightly lower than for the acetone and ethanol samples. For example, the T_c value of the toluene sample was 35.7 K, while the corresponding values for the acetone and ethanol samples were 37.2 K and 36.8 K, respectively. This depressed result for the toluene sample is considered to be due to its poor crystallinity, resulting in a significant amount of strain and crystal defects in the sample after ball milling.

4. Summary

We evaluated the effects of ball-milled B powders using different media, such as acetone, ethanol, and toluene, on the superconducting properties of MgB_2. It was observed that the *a* and *c* lattice parameters did not change for any of the samples, suggesting that C could not substitute into B sites during ball milling. Specifically, ball-milled B using toluene leads to smaller MgB_2 grains, resulting in enhanced J_c under high field. The estimated J_c was 5 x 10^3 A/cm^2 at 8 T and 5 K. This value is much higher than that of the pure reference MgB_2, by a factor of 20. At 20K, however, the $J_c(B)$ performance of the toluene sample is slightly worse than for the pure sample. This depressed value is probably related to the poor crystallinity. Further studies on the ball-milling process promise to allow adjustment of the desired phase form, such as for MgB_2 made with low grade boron powder via solid state reaction for future applications.

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List of Table

Figure Captions

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Table 1. X. XU et al.

	FWHM (deg.)			Lattice constant		
Samples	**(100)**	**(110)**	**(002)**	**a(Å)**	**c(Å)**	**c/a**
pure	0.4300	0.4860	0.4940	3.0848	3.5298	1.1442
Toluene	0.4640	0.6800	0.6800	3.0812	3.5244	1.1438
Ethanol	0.3620	0.4700	0.4700	3.0843	3.5292	1.1442
Acetone	0.3440	0.4560	0.4960	3.0830	3.5258	1.1436

Fig. 1. X. XU et al.

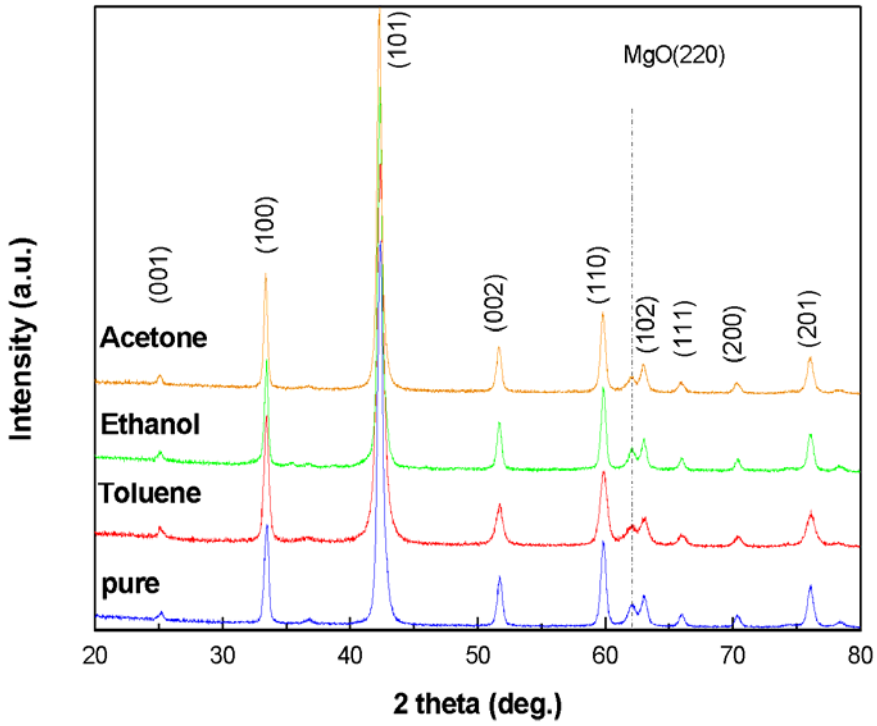

Fig 2. X. XU et al.

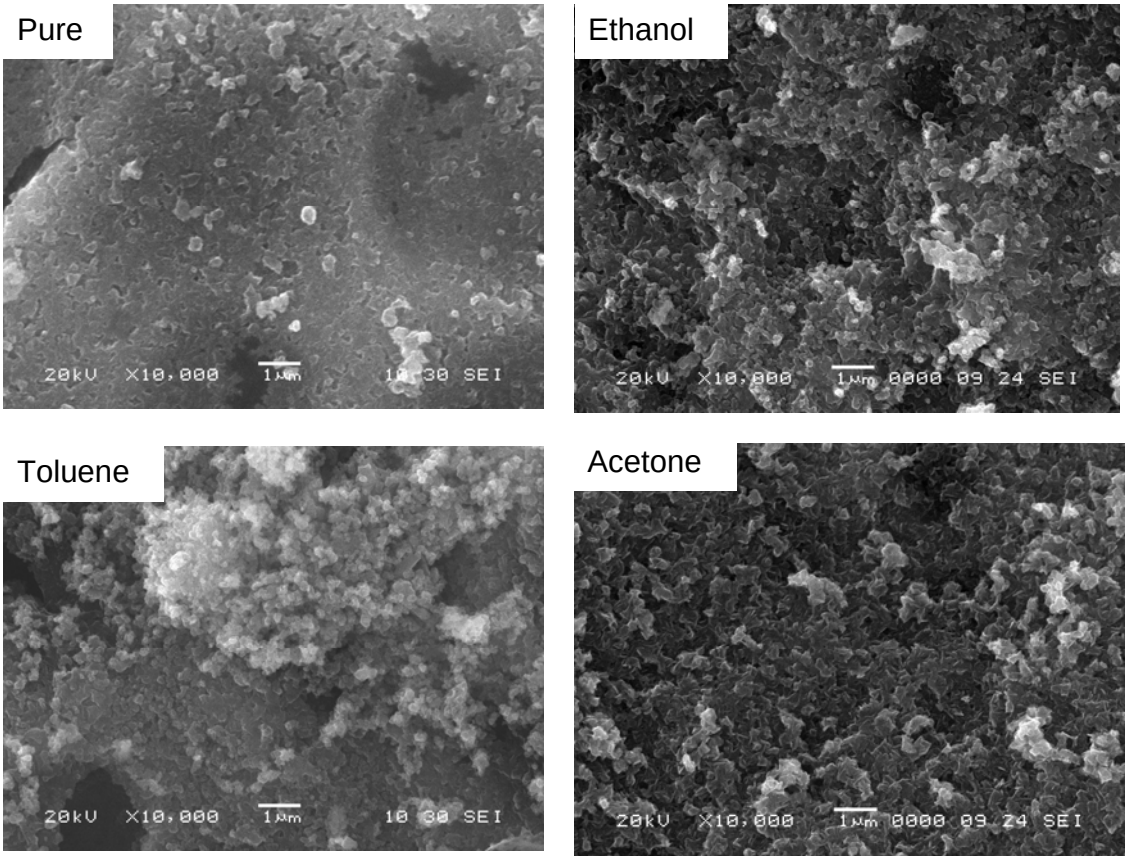

Fig 3. X. XU et al.

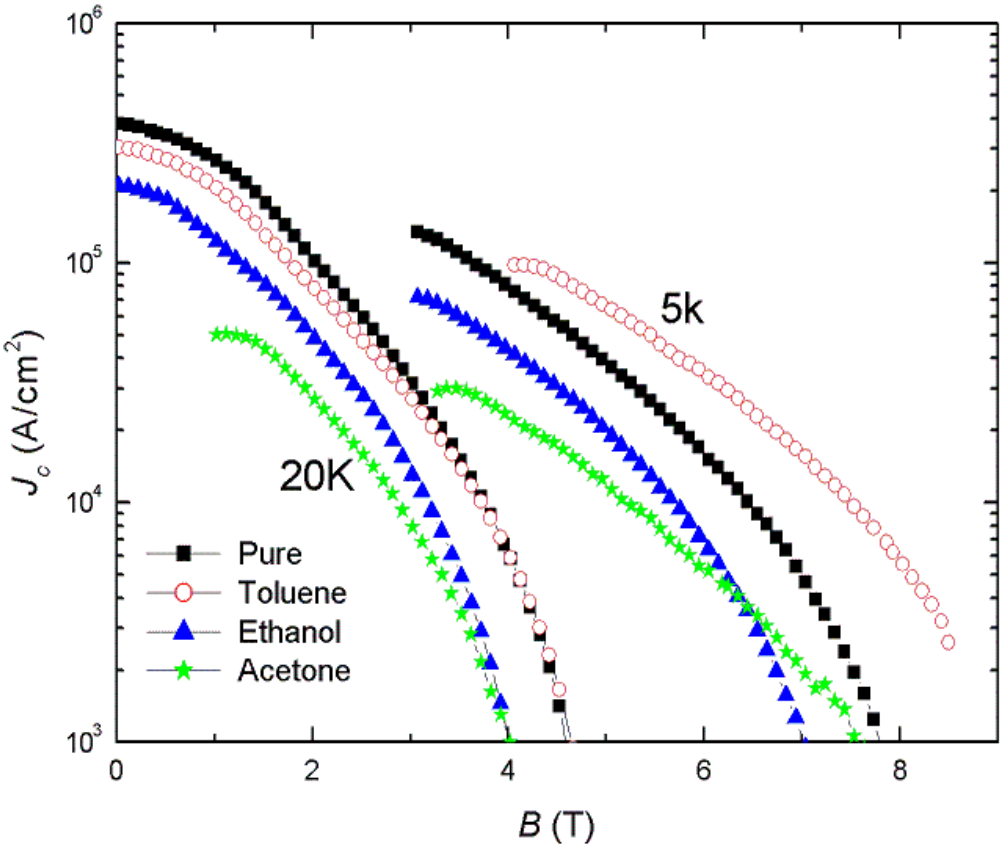

Fig 4. X. XU et al.