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# Superconducting $MgB_2$ ceramics and tapes prepared from mechanically milled powders

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Bulks and tapes of $MgB_2$ with 5 wt.% SiC were prepared from Mg, B and SiC. Mixing of the raw powders was performed in Ar atmosphere by high energy milling using a planetary mill. Number of balls (10 or 20), size (10 mm or 7 mm, respectively), rotation speed (200 rpm or 400 rpm) and milling time (up to 3 h) were varied. Powders were compared through XRD and SEM. From the as-prepared powders, bulk and tape samples were prepared and investigated by magnetic (SQUID) and transport (four-probe method) measurements. Results suggest that through variation of the milling conditions such as rotation speed, size and number of balls it is possible to control the value of the critical current density, $J_c$ and the slope of the $J_c(B)$ curve. For different heat treatment conditions milling with 400 rpm and using 20 balls of 7 mm always resulted in lower $J_c(B)$ than for the tapes or bulks produced from hand-milled mixture. Use of 10 balls of 10 mm keeping all the other conditions constant changed the slope of the $J_c(B)$ curve possibly improving $J_c$ above a crossover at 4 T. Mild milling with a rotation speed of 200 rpm (20 balls x 7 mm) resulted in enhancement of $J_c$ in the entire investigated region $B \leq 14$ T, but the slope was steeper than for the best sample produced from the hand-milled mixture and a crossover is likely to occur for $B > 14$ T leading to lower $J_c$-values. The best samples had at 4.2 K $J_c = 3.6 \times 10^2$ A·cm$^{-2}$ at 14 T and $J_c = 5 \times 10^3$ A·cm$^{-2}$ at 10 T.

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*Keywords*: $MgB_2$, superconductor, bulk, tape, milling, critical current density

## 1. Introduction

Magnesium diboride, $MgB_2$ is considered a promising candidate to replace low temperature superconductors (LTS) or to fill in niches of applications requiring intermediate characteristics between LTS and high temperature superconductors (HTS). Despite significant advantages such as non-toxicity, low density, it is composed of just two elements, it is cheap and available in large amount, it has 2 band gap energies that allow new physics in tuning or enhancing upper critical field, $MgB_2$ has also serious drawbacks such as poor mechanical properties, pinning properties in high magnetic fields has to be improved to compete with other superconductors, and reproducibility is somewhat low due to its high sensitivity to processing imposed especially by high volatility and oxygen reactivity of Mg. Several methods are used in the literature to overcome the problems. Among them additions of nano-powders such as SiC [1] was proven to work well in enhancing the critical current density, $J_c$. Another idea was to synthesize $MgB_2$ from fine mixtures of powders activated by high energy milling. Several articles [2-6] are showing an improvement in $J_c$ by this approach. Nevertheless our experiments on high energy milling in $H_2$ or Ar atmosphere [7] showed that the maximum $J_c$ is obtained for the hand-milled powder in Ar. Perner at all [4] noted that there is an optimum milling time to obtain $MgB_2$ with improved $J_c$. Matsumoto et al [5] obtained improvement of $J_c$ when using milled mixtures with Mg, but the use of $MgH_2$ instead of Mg led to the decrease of $J_c$ in the final product. It is clear that processing processes are rather complex and there are opposite effects affecting crystal quality, impurification, reactivity, morphology, defects. All of them significantly influence superconducting characteristics of $MgB_2$. Further research in this direction is of interest.

In a previous paper [8] we reported on the field-asisted sintering of $MgB_2$ superconductor doped by SiC and $B_4C$.

In this work we prepared bulk samples and tapes of $MgB_2$ using high energy milled mixtures of Mg, B and SiC in a planetary mill. Parameters such as milling time, rotation speed and number and size of balls were varied and their influence on $J_c$ was investigated.

## 2. Experimental

Mixtures of Mg (99.5% purity, ~45 μm average grain size), B (95 % purity, ~85 μm average grain size) and SiC (~20 nm) with composition $(Mg+B_2)_{0.95}(SiC)_{0.05}$ were prepared by hand mixing under Ar (glove-box) and by high energy mechanical milling in a planetary ball mill (Fritsch P7, Cr-steel pot). Milling was done in Ar gas introduced at 1.7 atm into evacuated milling pot. Milling time (tm) was 0.5, 1 and 3 h. We used balls of the same material as the pot, but their size and number was (7 mm ×20) or (10 mm × 10) for the same amount of loaded powder. Rotation speed was 200 and 400 rpm.

As-milled mixtures were pressed into pellets or they were loaded into Fe-tubes (inner and outer diameters of 3.3 and 6 mm, respectively). After groove rolling down to 2 mm ×2 mm for a square cross section, subsequent flat rolling into a tape of 4 mm ×0.5mm was applied. Samples

were wrapped into Zr-foil and annealed in Ar. Samples and processing conditions are presented in Table 1.

X-ray diffraction was measured on as-milled powders and $MgB_2$ reacted samples (PANalytical/Phillips, CuKα radiation). Microstructure of the samples was observed by scanning electron microscopy SEM (JEOL JSM 6400F).

Critical current density $J_c^{M-B}$ up to 4 T was estimated from magnetization loops M-B measured with a SQUID (Quantum Design, 5 T) magnetometer considering the loop width ΔM and applying Bean model [9] $J_c = 30\Delta M/d$, with d = average grain size determined from SEM observations. Using the same magnetometer critical temperature was taken as the onset of the diamagnetic signal in the zero-field-cooled M(T) curves measured for a *dc* magnetic field of 20 Oe. For the tapes critical current density $J_c^{transport}$ was obtained from the four-probe standard current-voltage I-V measurements for a criterion of 0.1 μV/cm. The distance between voltage contacts was 1 cm for a sample length of 4cm. Magnetic field was applied using a 15 T magnet installed at High Field Laboratory for Superconducting Materials, Tohoku University.

*Table 1. Samples and processing conditions. Samples A-F are milled powder mixtures. Notations with t and b stand for tapes and bulk samples, respectively.*

| Sample | Milling (time (tm) / size x No balls / rotation speed | Heat treatment Temperature./time |
|---|---|---|
| A | hand | - |
| B | 0.5 h/7 mm x 20/400 rpm | - |
| C | 1 h/7 mm x 20/400 rpm | - |
| D | 3 h/7 mm x 20/400 rpm | - |
| E | 0.5 h/10 mm x 10/400 rpm | - |
| F | 0.5 h/7 mm x 20/200 rpm | - |
| At1 | As for A | 650°C/0.5 h |
| At2 | As for A | 650°C/3 h |
| At3 | As for A | 700°C/0.5 h |
| At4 | As for A | 700°C/1 h |
| At5 | As for A | 700°C/3 h |
| At6 | As for A | 750°C/0.5 h |
| At7 | As for A | 750°C/3 h |
| Bt | As for B | 700°C/0.5 h |
| Ct | As for C | 700°C/1 h |
| Et | As for E | 700°C/0.5 h |
| Ft | As for F | 700°C/0.5 h |
| Ab | As for A | 700°C/1 h |
| Bb | As for B | 700°C/1 h |
| Cb | As for C | 700°C/1 h |
| Db | As for D | 700°C/1 h |

## 3. Results and discussion

XRD and SEM data for as-milled mixtures A-D are presented in Figs 1 and 2. In Fig. 1 are also shown SEM images for the raw powders. One can observe that all powders agglomerate except for Mg that is composed of large particles. Agglomerates are up to 30-50 μm in diameter and samples A-D look alike. Essential differences were found in XRD patterns (Fig. 2): enhancement of the milling time produces patterns with Mg-lines of lower intensity and larger *full width at half maximum* (FWHM). FWHM was estimated at 0.16°, 0.23°, 0.25° and 0.27° for A-D mixtures respectively. This indicates smaller grains and imperfect crystallinity for Mg vs. milling time (Table 1). A relatively short time milling produces a fast decrease of FWHM and for longer time the decrease is slower. Boron cannot be observed in the XRD patterns due to its small particle size and amorphous state.

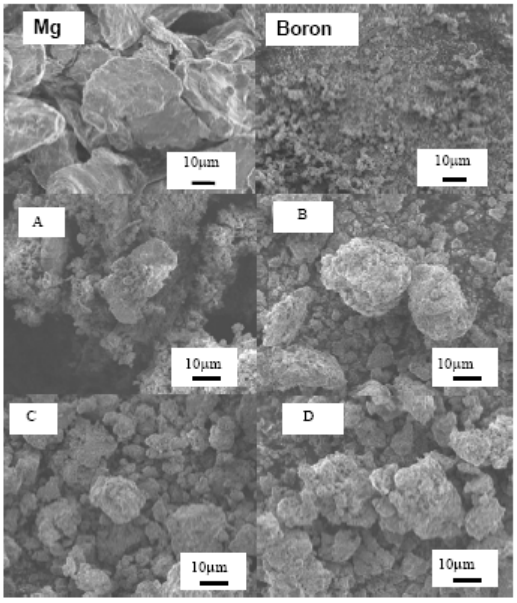


*Fig. 1. SEM images of the raw powders Mg and Boron and of the milled samples A-D (see Table 1).*

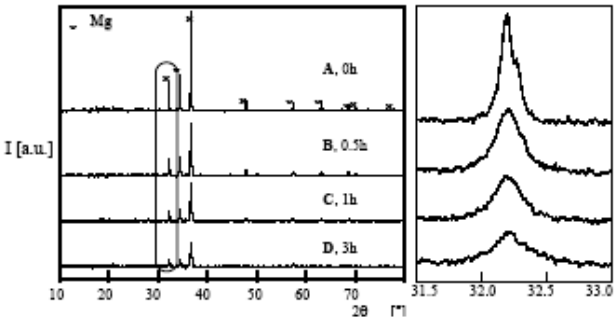


*Fig. 2. XRD patterns for A-D powders and a detail showing (100) peak for Mg.*

Bulk samples Ab-Db prepared from the mixtures A-D and for the same heat treatment conditions (700°C/1 h) have very different $T_c$ and $J_c$. Critical temperature was 37.4, 34.8, 32.2 and 32 K for Ab-Db, respectively. The decrease in $T_c$ vs. milling time seems to follow the same tendency as FWHM for A-D samples vs. milling time. Lower crystal quality of Mg resulting from different milling time deteriorates the quality of the $MgB_2$ samples. XRD patterns

for Ab-Db samples are similar (data are not shown) and intensity and FWHM of $MgB_2$ diffraction lines decrease with milling time. Results are suggesting that there is a direct relationship between the Mg status after milling and the final quality of $MgB_2$. Although an explanation cannot be expressed based on the current data, it is probable that Mg status influences growth and doping processes of $MgB_2$, and, hence the superconducting characteristics of the final product. Further detailed investigations are necessary in this direction. Impurity phases observed in the XRD patterns of the Ab-Db samples were $Mg_2Si$, MgO and traces of $MgB_4$. Some residual Mg was detected in the Ab and Bb samples. SEM images of Bb-Db samples (Fig. 3) show uniform morphology composed of fine particles and micrometer-order agglomerates. Uniformity and packing are better for the samples that experienced milling for a shorter time. This translates into worsening of the connectivity for milled samples and can induce the decrease of $J_c(B)$ with milling time (Fig. 4). This tendency of $J_c(B)$ is valid at low (4.2 K) as well as high temperatures (20 K).

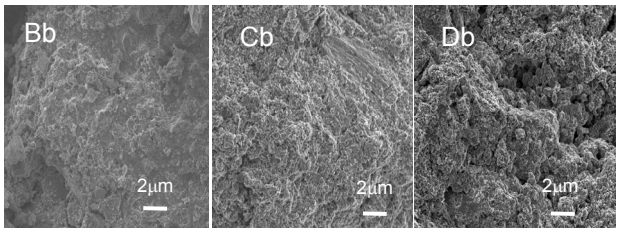


*Fig. 3 SEM images taken on fractured surface of Bb-Db bulk $MgB_2$ samples.*

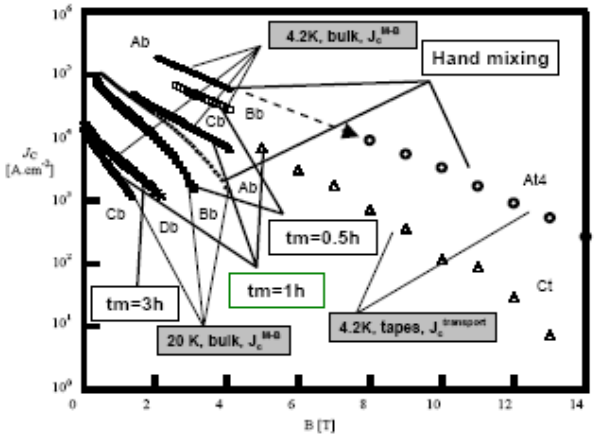


*Fig. 4 $J_c(B)$ curves for bulk samples Ab-Db and tapes At4 and Ct (annealed at 700 °C for 1 h). Milling time tm and temperature of the $J_c$ measurements are indicated.*

In Fig. 4 are also plotted $J_c(B)$ curves for two tapes (At4 and Ct, Table1). Data are consistent with results for bulk samples Ab-Db: the tape (At4) fabricated from the hand mixed powder has a higher $J_c(B)$ than the tape (Ct) from milled powder (tm = 1 h). In addition the extrapolated values for bulks and tapes are approximately matching each other (slightly higher for the tapes probably due to higher evaporation loss of Mg for the bulk and also due to the differences between the two types of measurements, i.e. M-B and transport for bulks an tapes, respectively).

Before discussing further milling experiments it is noteworthy that the heat treatment condition 700 °C for 1 h was selected as being the optimum one (tape At4) so that $J_c$ is maximum (see tapes At1-At7 in Fig. 5 and Table 1). Tapes At1-At7 (Fig. 5) were fabricated from the hand milled powder mixtures. Up-to-date and to our knowledge the record high absolute values of $J_c(B)$ are for nano-SiC [1] and for C-nano [10] doped $MgB_2$ tapes fabricated at 650 °C for 1 h and at 750 °C for 1 h, respectively. $J_c(B)$ data for these two tapes are also plotted in Fig. 5. Authors of ref. 1 insisted that the type of the dopant is very important: nano-SiC is a dopant that can have a reaction and C-substitution for Boron at the same temperature as $MgB_2$ formation (650 °C), while nano-C needs significantly higher temperatures, usually 900-1000 °C although, as already mentioned, very good results were obtained for nano-C doped tapes reacted at 750 °C. Our best tape At4 made from hand mixed powders was fabricated at optimized temperature of 700 °C for 1 h. This temperature is higher than 650 °C, but we also used nano-SiC powder of 20-30 nm as in ref. [1].

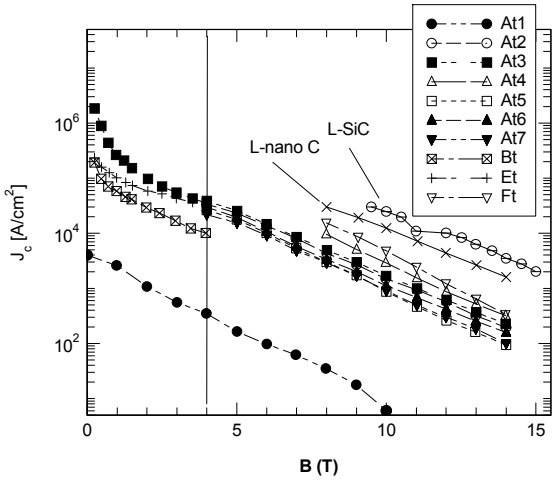


***Fig. 5*** *$J_c(B)$ curves for tapes (see Table 1). Samples denoted L-SiC and L- nano C are record $J_c(B)$ tapes from refs [1] and [9], respectively. Curves of $J_c(B)$ at $B \leq 4$ T (except for At1) are obtained from M-B loops measured on the $MgB_2$-core of the tape after removal of Fe-sheath.*

The above results suggest that the image on dopants proposed in ref. [1] is not complete. There is a fine interplay between dopant material and raw materials, mixture characteristics, heat treatment and superconducting properties. Parameters such as type, purity, crystal quality, particle size, distribution and morphology of the raw materials including dopant as well as the uniformity and reactivity of the initial powder mixtures have to be controlled and correlated with heat treatment conditions to maximize and reproducibly control properties. Following this idea we have tried to modify milling parameters and

results are addressed in the next paragraph. Another piece of information is that for our best tape At4 the amount of SiC is 5 %wt. This means that the amount of available C for doping into $MgB_2$ is lower than in the tapes from refs [1, 9] with record high $J_c$ (10 % wt. of SiC and 5 % wt. of nano-C). Noted difference might be one reason explaining lower $J_c$ for our tapes. Relatively low purity of B might be also a problem in this regard.

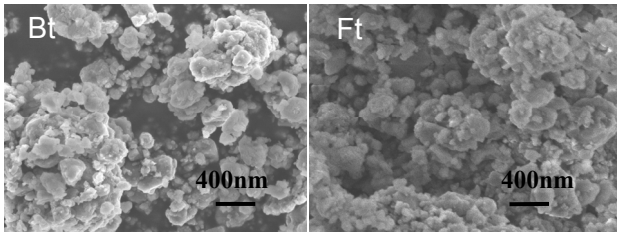


*Fig. 6. SEM images of the $MgB_2$ core extracted from the tapes Bt and Ft that were fabricated from mixtures milled for 0.5 h with 20 balls of 7 mm and 10 balls of 10 mm, respectively.*

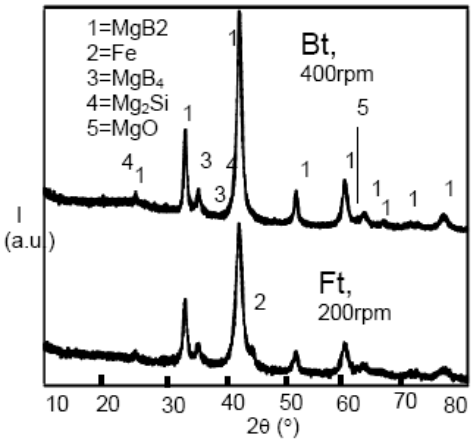


*Fig. 7 XRD patterns on powders obtained by grinding the ceramic core of the tapes Bt and Ft. The peaks of Fe were largely contributed from the Fe sheath.*

Tapes Bt and Et were fabricated for the same annealing conditions (700 °C for 0.5 h) from mixtures milled with 20 balls of 7 mm (B) or 10 balls of 10 mm (E). Second sample Et has better $J_c(B)$ values than for the sample Bt (Fig. 5). However, in the field range of $B \leq 4$ T $J_c(B)$ for tape Et is lower than for the tape (At3) fabricated from the hand mixed powder (A). Nevertheless, $J_c(B)$ curves of Et and At3 cross each other at around $B \approx 4$ T so that at higher fields $J_c$ of sample Et is likely superior to that of At3 (Fig. 5). We conclude that the slope of the $J_c(B)$ depends on milling conditions. The differences in XRD and SEM between as-milled mixtures B and E and also between tapes Bt and Et were too small to give an explanation for the observed $J_c(B)$ differences. Another experiment supporting previous conclusion is the following: using powders A and F, i.e. mixtures milled with 400 rpm and 200 rpm, tapes At4 and Ft were fabricated at 700 °C for 1 h. Mild milling for tape Ft resulted in enhancement of $J_c$ and this is our best tape for $B \leq 14$ T (Fig. 5). This positive result is shadowed by the fact that the slope of $J_c(B)$ curve is steeper than for our At4 tape or for the tapes with record $J_c$ reported in [1] and [9] so that at fields above 14 T $J_c$ of Ft will likely be lower than for At4. The differences in SEM (Fig. 6) and XRD (Fig. 7) are again very small to allow further analysis and more experiments are necessary.

## 4. Conclusion

In summary tapes and bulk samples of SiC-doped $MgB_2$ superconductor were fabricated from milled mixtures. It is shown that milling conditions such as rotation speed and size and number of balls can influence $J_c$ values and the slope of $J_c(B)$ curves. The reason for such behavior is not clear, but results suggest that there is a fine interplay between raw materials, milling processing, heat treatment and superconducting characteristics of the final product. To enhance $J_c$ one has to find optimum processing conditions including for milling.

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