Excess Mg in situ powder addition for enhancing critical current density of ex situ MgB$_2$

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Abstract
In this work, ex situ MgB$_2$ bulks were added with (1.5 Mg + 2B) and sintered in an attempt to enhance its intergrain connectivity. The addition was varied within the range of 0–50 wt.%, and the sintering was undertaken at 700 °C, 800 °C, and 1000 °C, respectively, for 1 h. Superconducting critical temperature, $T_c$ of the samples was determined to be around 38 K as shown by the temperature dependence of susceptibility measurement. It was found that critical current density, $J_c$ increased with the increased amount of the addition. $J_c$ was further enhanced to $2 \times 10^4$ A cm$^{-2}$ (0 T, 20 K) as the sintering temperature was raised. The increase of $J_c$ is due to improved grain coupling as a result of in situ formation of MgB$_2$, which fills the voids and connects the ex situ MgB$_2$ grains. Additionally, the grain coupling was further strengthened by solid-state self-sintering at higher temperatures. The increment of $J_c$ was accompanied by a narrower width of double-step transition of $T_c$ attributable to a more complete MgB$_2$ phase formation of the samples as the sintering temperature was increased.
1 Introduction

Superconducting critical temperature, \( T_c \approx 39 \text{ K} \) of magnesium diboride, \( \text{MgB}_2 \), is one of the highest among the non-cuprate-based superconductors [1]. Like other superconducting compounds such as high-temperature superconductors (HTS) [2–5] and the iron-based one [6], \( \text{MgB}_2 \) has a great potential for practical applications, especially in liquid helium-free temperatures (15–20 K). Besides, \( \text{MgB}_2 \) consists of two light elements of magnesium (Mg) and boron (B) which are relatively inexpensive as compared to those used to synthesize iron-based and HTS. Other features such as weak-link free behavior across grain boundaries, larger coherence length, and lower electronic anisotropy [7–10] are the additional advantages of \( \text{MgB}_2 \).

Two common approaches for preparing \( \text{MgB}_2 \) bulk samples are in situ [11–14], and ex situ [15–17] methods. For in situ reaction process, Mg grains melt and diffuse into B grains to form \( \text{MgB}_2 \) through liquid–solid reaction during heat treatment. The sample prepared by this method yields a strong intergrain coupling and can easily attain high critical current density, \( J_c \). Similar to the cuprate HTS [18–20], the addition of impurities into \( \text{MgB}_2 \) during the in situ reaction enhances \( J_c \) enormously [7, 21]. Due to the liquid–solid reaction, Mg sites turn into voids resulting in a low bulk density (\( \approx 50\% \)) [9]. On the other hand, a much higher packing factor of about 75% can be achieved in ex situ \( \text{MgB}_2 \), which is a pre-reacted \( \text{MgB}_2 \) prepared via the in situ reaction. Nevertheless, intergrain coupling of ex situ \( \text{MgB}_2 \) samples is much weaker than that of the in situ ones [9, 22].

Hence, we are motivated to improve the intergrain connectivity of ex-situ \( \text{MgB}_2 \) in an attempt to enhance its \( J_c \). To do so, ex situ \( \text{MgB}_2 \) was mixed with a mixture of Mg and B according to the proportion of (1.5Mg + 2B). This means of powder technology is cost-effective as no additional chemical dopants are required. The addition of mixed powder (1.5Mg + 2B) during in situ reaction is expected to strengthen the grain connectivity of ex situ \( \text{MgB}_2 \) due to the higher bulk density of ex situ \( \text{MgB}_2 \) [23]. To study the effect of (1.5Mg + 2B) addition on \( T_c \) and \( J_c \), the amount

Keywords Ex situ \( \text{MgB}_2 \) · In situ \( \text{MgB}_2 \) · Sintering · Superconducting transition · Critical current density
of the addition was varied according to $x$ (wt %) = 0, 10, 30, and 50 for sintering at 700 °C for 1 h. Another batch of samples was prepared by adding 30 wt.% of (1.5 Mg + 2 B) into the ex situ MgB$_2$ powder and sintered at 700 °C, 800 °C, and 1000 °C, respectively, for 1 h. The purpose of the heat treatment is twofold: (i) for ex situ MgB$_2$, it is expected to increase the cross-section of the grain-to-grain current path through solid-state self-sintering [15] (ii) for in situ MgB$_2$, it optimizes formation of MgB$_2$ phase, which in turn assists grain connectivity [24] in (i). Excess Mg was used in the mixed (1.5Mg + 2B) to compensate for Mg loss due to the high volatility of Mg at elevated temperatures.

2 Experimental details

Commercially available MgB$_2$ powder (Alfa Aesar, 99.0% purity) was used to serve as ex situ MgB$_2$. Varying amounts ($x$ weight percentage, wt.%, for $x = 0, 10, 30, \text{and} 50$) of mixed magnesium, Mg (Tangshan Wei Hao, 99.0% purity) and boron, B (Tangshan Wei Hao, 97.0% purity) powders with a molar ratio of 1.5:2 (Mg: B) were added to the ex situ MgB$_2$ powder and ground for 1 h in open air. The mixture was pressed into circular pellets with dimensions of ~13 mm diameter and ~1 mm thickness using a hydraulic press under a pressure of five tons. Then, the pellets were loaded into stainless-steel tube, and both ends of the tube were sealed. Finally, the tube was loaded into a tube furnace for heat treatment at 700 °C, 800 °C, and 1000 °C, respectively, for 1 h under a constant argon gas flow.

The samples were checked by X-ray diffraction (XRD) method using the PW 3040/60 MPD X’pert Pro Panalytical Philips DY 1861 X-ray diffractometer with Cu-K$_a$ radiation source ($\lambda = 1.5406$ Å). The scanning was carried out in the $2\theta$ range of 20°–80° with the increment step size of 0.03°. Microstructure imaging was performed using a scanning electron microscope (SEM-LEO 1455 VPSEM). Superconducting critical temperature, $T_c$, and critical current density, $J_c$, was measured using a SQUID magnetometer (Quantum Design: MPMS5). $T_c$ was measured using zero-field cooled conditions from 10 to 50 K under an applied field of 10 Oe. Magnetization hysteresis (M-H) loops were acquired in applied magnetic fields from 0 to +3 T at 20 K. $J_c$ of the bulk samples with dimensions of approximately 1.0 × 1.0 × 0.5 mm$^3$ was calculated from the M-H loops based on the extended Bean critical state model equation [25]:

$$J_c = \frac{20 \Delta m}{a^2d - (a/3)}$$

where $d$ is the sample thickness, $a$, $b$ ($a < b$) are cross-sectional dimensions of a rectangular sample and $\Delta m$ (in emu units, 1 emu $= 10^{-3} \text{ A m}^2$) is the hysteresis loop width.

3 Results and discussion

3.1 X-ray diffraction (XRD) analysis

Figure 1 shows XRD patterns of the ex situ MgB$_2$ samples and that added with $x$ wt.% of (1.5Mg + 2B) ($x = 0, 10, 30$)

![Fig. 1 XRD patterns of ex situ MgB$_2$ added with different weight percentages of (1.5Mg + 2B) and sintered at 700 °C for 1 h. The minor peaks were labeled as black diamond suit: MgO and black club suit: MgB$_4$.](image-url)
and 50). XRD patterns of the ex situ MgB$_2$ samples added with 30 wt.% of (1.5 Mg + 2 B) and sintered at different temperatures for 1 h are shown in Fig. 2. Majority of the diffraction peaks (Fig. 1 and Fig. 2) were indexed to MgB$_2$ phase (ICSD: 98-010-6149), having hexagonal crystal structure with P6/mmm space group. MgB$_2$ peak with the highest intensity was observed at 2$\theta$ $\approx$ 42.4° which corresponds to the (1 0 1) plane.

Some minor peaks observed at 2$\theta$ $\approx$ 62.2° and 78.6° were indexed to MgO (ICSD: 98-009-4096) in all the samples (Figs. 1 and 2). Intensity of these peaks increased with the increasing addition amount of (1.5 Mg + 2B). For the sample added with 30 wt.% of (1.5 Mg + 2B) and sintered at 1000 °C, MgO peak was clearly observed at 2$\theta$ $\approx$ 42.9° which is near the (1 0 1) peak of MgB$_2$ at 2$\theta$ $\approx$ 42.4° (Fig. 2) indicating the presence of significant fraction of MgO in the sample. In addition to the MgB$_2$ and MgO phases, a peak with a weak intensity corresponding to MgB$_4$ (ICSD: 98–009-1660) at 2$\theta$ $\approx$ 45.9° was noticeable for the ex-situ sample sintered at 700 °C for 1 h (Fig. 1) and the samples added with 30 wt.% of (1.5Mg + 2B) and sintered at 800 °C for 1 h (Fig. 2). However, multiple peaks of MgB$_4$ (ICSD: 98-009-1660) appeared in the XRD pattern of the sample added with 30 wt.% of (1.5Mg + 2B) and sintered at a higher temperature of 1000 °C (Fig. 2). Without an excessive amount of MgO and MgB$_4$, the presence of these phases may assist in pinning the movement of flux lines for enabling the samples to carry high $J_c$ [26, 27].

Tables 1, 2 show intensity fractions of the phases formed and lattice parameters of $a$ and $c$ axis for all the samples. The intensity fractions were estimated using the following formula [28–30]:

$$\text{MgB}_2(\%) = \frac{\sum I_{\text{MgB}_2}}{\sum I_{\text{MgB}_2} + \sum I_{\text{MgO}} + \sum I_{\text{Other}}} \times 100\%,$$

where $I$ is the peak intensity of the respective phases. As shown in Table 1, the intensity fraction of MgB$_2$ phase changes very little between 97 and 98% with addition of up to 50 wt.% of (1.5Mg + 2B). The slight decrease was probably due to the availability of more Mg [from the mixture of (1.5Mg + 2B)], thus increasing the formation of MgO.

Fig. 2 XRD patterns of ex situ MgB$_2$ added with 30 wt.% (1.5Mg + 2B) and sintered at different temperatures for 1 h. The minor peaks were labeled as black diamond suit: MgO and black club suit: MgB$_4$

| X wt.% (1.5Mg + 2B) | Intensity fraction (%) | Lattice parameters |
|---------------------|------------------------|-------------------|
|                     | MgB$_2$ (ICSD: 98-010-6149) | MgO (ICSD: 98-009-4096) | MgB$_4$ (ICSD: 98-009-1660) |
| 0                   | 98.4                   | 1.5               | 0.1                  |
| 10                  | 98.8                   | 1.2               | 0.0                  |
| 30                  | 97.6                   | 2.4               | 0.0                  |
| 50                  | 97.2                   | 2.8               | 0.0                  |

Table 1 Intensity fraction of the phases formed and lattice parameters for ex situ MgB$_2$ were added with different weight percentages of (1.5Mg + 2B) and sintered at 700 °C for 1 h
Table 2: Intensity fraction of the phases formed and lattice parameters for ex-situ MgB$_2$ added with 30 wt.% (1.5Mg + 2B) and sintered at different temperatures for 1 h

| Sintering temperature (°C) | Intensity fraction (%) | Lattice parameters |  |
|---------------------------|------------------------|--------------------|---|
|                           | MgB$_2$ (ICSD: 98-010-6149) | MgO (ICSD: 98-009-4096) | MgB$_4$ (ICSD: 98-009-1660) |
| 700                       | 97.6                   | 2.4                | 0.0                        | a axis (Å) | c axis (Å) | c/a |
|                           | 3.0848 ± 0.0001        | 3.5238 ± 0.0002    | 1.1423                     |
| 800                       | 97.2                   | 2.8                | 0.1                        | 3.0843 ± 0.0002    | 3.5236 ± 0.0002    | 1.1424 |
| 1000                      | 68.0                   | 16.7               | 15.3                       | 3.0834 ± 0.0002    | 3.5236 ± 0.0002    | 1.1428 |

With the addition of (1.5Mg + 2B), the formation of MgB$_4$ did not occur (Table 1). This suggests that the (1.5Mg + 2B) addition increased partial pressure of Mg (due to the Mg there) and thus suppressed decomposition of MgB$_2$ into MgB$_4$ and Mg [31–33]. Unit cell lattice parameter of a axis is larger for the sample with addition of 50 wt.% of (1.5Mg + 2B). While considering the c axis lattice parameter, its value increased starting from the addition level of 30 wt.% of (1.5Mg + 2B). Consequently, the ratio of the c axis to a axis (c/a) is larger. The increase in the lattice parameters may be associated with in situ formation of MgB$_2$ as a result of the addition of (1.5Mg + 2B) into the ex situ powder leading to buckling in the unit cell of MgB$_2$.

For the ex situ MgB$_2$ added with 30 wt.% (1.5Mg + 2B), increasing the sintering temperature from 700 °C to 1000 °C abruptly decreased MgB$_2$ phase from 97.6 to 68.0% (Table 2). The decrease in MgB$_2$ phase is due to the increase of both MgO and MgB$_4$ phases. At higher sintering temperatures, MgB$_2$ decomposed into MgB$_4$ and Mg [15, 32, 34] giving rise to the availability of more Mg to react with oxygen to form MgO. These processes were accelerated as the sintering temperature was increased. As shown in Table 2, the intensity fraction of MgB$_4$ phase increased from 0.0 to 15.3% as the sintering temperature was raised from 700 °C to 1000 °C. Concurrently, the intensity fraction of MgO increased from 2.4 to 16.7%. The chemical reaction equation below shows the decomposition of MgB$_2$ to MgB$_4$ and Mg [35]:

\[
2\text{MgB}_2(s) \rightarrow \text{MgB}_4(s) + \text{Mg}(g).
\]

While the c axis lattice parameter remained relatively unchanged as the sintering temperature was raised from 700 to 1000 °C, the a axis decreased more significantly for the samples sintered at 1000 °C (Table 2). Accordingly, the ratio c/a increased with the sintering temperature. This behavior may be related to strain resulting from the presence of considerable fraction of impurity phases [36].

3.2 Microstructure analysis

Figure 3 shows SEM images taken on the fractured surfaces of the samples at a magnification of 5000 X. As can be observed from the images, the samples show randomly oriented grains with irregular shapes. Voids (dark regions) between the grains can be clearly seen for 0 wt.% added sample (Fig. 3a). However, the gap between the voids appeared to be reduced as the addition level and the sintering temperature increased (Fig. 3b, c, d, e, f and g), suggesting an improvement of grain coupling for the samples. It is known that the presence of voids will reduce the bulk density and disrupt the grain connectivity of the samples leading to a reduction of $J_c$ [37, 38]. As the amount of the addition was increased, the samples appeared to be less porous most probably due to the in situ formation of MgB$_2$ from the addition of (1.5Mg + 2B) that filled some of the voids [39].

Figure 3 right shows the grain size distribution of the samples. The grain size distribution was calculated from the randomly selected 100 grains according to the SEM images using the Image-J software. Overall, the average grain size of (1.5Mg + 2B) added sample varied slightly only within the range of 0.52 µm–0.56 µm (Fig. 4b–d) as compared with 0.50 µm of the 0 wt.% added sample (Fig. 4a). This result agrees with the previous finding that no significant change in the grain size was observed for the ex situ MgB$_2$ sintered at 900 °C for even up to 240 h [15]. The slight increase in the average grain size may be due to Mg melting at around 650 °C resulting in neck formation and aggregation between the grains [16] leading to grain growth. Besides, Mg melting plays an important role in cleaning grain boundaries and healing microcracks which enhance grain connectivity of the samples [40–42]. For the samples added with 30 wt.% of (1.5Mg + 2B), the average grain size decreased slightly from 0.52 to 0.48 µm as the sintering temperature was increased from 700 to 1000 °C. Such a small decrease may be linked to Mg deficiency caused by Mg loss at the higher sintering temperature [43]. With the increase in the addition levels and the sintering temperatures, the reduction in the average grain size (Fig. 4) may contribute to the enhancement of $J_c$ as a result of the increased number of grain boundaries for flux pinning [42].

3.3 Superconducting analysis

3.3.1 Critical temperature, $T_c$

Figure 5a, b shows the temperature dependence of magnetic susceptibility between 10 and 50 K for all the samples. In
order to determine onset ($T_{c\text{-onset}}$), onset of the second transition, $T_{c\text{-onset2}}$, and offset ($T_{c\text{-offset}}$) of superconducting critical temperature, derivatives of the magnetic susceptibility with respect to the temperature ($\delta \chi/\delta T$) versus temperature were plotted and shown in Fig. 5c, d. As shown in Table 3, all the samples show a $T_{c\text{-onset}} \approx 38$ K. Such a minor variation in $T_{c\text{-onset}}$ among the samples indicates that the addition of (1.5Mg + 2B) powder did not give rise to significant perturbation in the electronic structure of MgB$_2$ [44]. $T_{c\text{-onset2}}$ was determined from the peak at the lower temperature as shown in Fig. 5c, d. $T_{c\text{-onset2}}$ is 30 K and 33 K for the 30 wt.% and 50 wt.% added sample, respectively (Table 3). For the samples sintered at 700 °C for 1 h (Fig. 5a), the addition of a higher amount of (1.5Mg + 2B) (30 wt.% and 50 wt.%) resulted in a double-step transition. The double-step transition indicates inhomogeneity within the samples [22], which may be caused by the incomplete reaction between Mg and B during the heat treatment after the addition of (1.5Mg + 2B). The presence of ex situ MgB$_2$ particles may slow down MgB$_2$ phase formation as they hinder the diffusion of Mg and B in the mixture. Moreover, the width transition, $\Delta T_c$ ($T_{c\text{-onset}} - T_{c\text{-offset}}$) of the 30 wt.% sample is larger.
Fig. 3 (continued)
than that of the 50 wt.% one. The larger $\Delta T_c$ of the former suggests the presence of a higher density of defects in the sample. Similar double-step transition was also observed in the 30 wt.% of (1.5Mg + 2B) added samples sintered at 800 °C and 1000 °C. Nevertheless, the transition width was narrower, and the double-step transition became less obvious as the sintering temperature was increased to 1000 °C. The narrower transition width with the increasing sintering temperature implies more complete MgB$_2$ formation consistent with the increment of $J_c$ (which will be discussed in the following section).

### 3.3.2 Critical current density, $J_c$, and pinning force

Figure 6 shows the $M$–$H$ loops of the samples measured at 20 K after zero-field cooling. Flux jump is not apparent as evidenced from the loops. The width of the loops, $\Delta M$ is larger reflecting increment of $J_c$ as the addition level and the sintering temperature increases. Figure 7 shows the dependency of $J_c$ on the applied magnetic fields from 0 to 3 T at 20 K. Self-field $J_c$ for the 0 wt.% added (1.5Mg + 2B) sample is 3.0 kA cm$^{-2}$. When 10 wt.% of (1.5 Mg + 2 B) was introduced into the sample, self-field $J_c$ increased slightly to 3.8 kA cm$^{-2}$. A sudden increase in self-field $J_c$ (10.0 kA cm$^{-2}$) was observed in the sample added with 30 wt.% (1.5Mg + 2B). The value of self-field $J_c$ continued to increase to 13.1 kA cm$^{-2}$ with an addition of 50 wt.% (1.5Mg+2B). As shown in Fig. 7a, a significant enhancement of $J_c$ is seen over the field range 0–3 T after the addition of 30 wt.% of (1.5Mg + 2B). The increase in $J_c$ can be associated with a reduction in the dimensions of voids between the particles, thereby resulting in increased number of contact points among the grains which in turn improved the intergranular grain coupling [15, 16]. Apart from this, in situ formation of MgB$_2$ also helped in connecting the ex situ MgB$_2$ grains. The enhanced $J_c$ versus field for both the 30 wt.% and 50 wt.% added samples coincide with the appearance of the double-step transition (Fig. 5a) manifesting the presence of a higher fraction of defects for flux pinning as a result of the increased addition of (1.5Mg + 2B).

For the 30 wt.% (1.5Mg + 2B) added samples, self-field $J_c$ (20 K) increased from 10.0 kA cm$^{-2}$ to 20.7 kA cm$^{-2}$ when the sintering temperature was raised from 700 to 1000 °C, respectively. However, at a higher field, the $J_c$ value of the sample sintered at 800 °C is lower than that sintered at 700 °C (Fig. 7b). This could be due to lower defect density as indicated by the smaller $\Delta T_c$ of the sample (Table 3).

Consequently, flux pinning contributed by the defects was reduced and thus decreased $J_c$. Moreover, the $J_c$ also showed a stronger dependency on the applied field. As the sintering temperature was increased to 1000 °C, $J_c$ was enhanced, because grain coupling was further reinforced through solid-state self-sintering [15] in addition to voids filling and grain connectivity assisted by in situ formation of MgB$_2$. This is consistent with the narrower transition width, $\Delta T_c$ (Fig. 5b) indicating improved homogeneity leading to enhanced grain coupling of the sample. It is noteworthy that $J_c$ of the sample sintered at 1000 °C is the highest despite its lowest fraction of MgB$_2$ (68.0%) (Table 2). This indicates that the $J_c$ can be further increased by optimization of heat treatment and material processing conditions. By doing so, it is anticipated the grain coupling can be further strengthened while reducing the impurities considerably. On the other hand, it should be noted that non-superconducting phases can also serve as flux pinning centers. Table 4 compares $J_c$'s of the best sample from this study and that of other reported work on the addition of Mg into in situ and ex situ MgB$_2$.

Figure 8 shows normalized flux pinning force, $F_p/F_{p,\text{max}}$ as a function of reduced field, $h = H/H_{irr}$ at 20 K. The irreversibility field, $H_{irr}$ was determined from the $M$–$H$ loops using the criterion of $J_c = 100$ A cm$^{-2}$ [47, 48]. Curve fitting was undertaken using the software Origin in order to better estimate the peak value of $h$, $h_{\text{peak}}$. As shown in Table 5, $h_{\text{peak}}$ for the sample without addition is 0.34 indicating the dominant pinning mechanism of normal core [49] which may originate from the non-superconducting inhomogeneity in the commercial MgB$_2$ powder [50]. The inhomogeneity was worsened after the sintering process [50]. As reported by Tanaka et al., their sintered ex situ MgB$_2$ (homemade) with better homogeneity showed $h_{\text{peak}} \approx 0.2$ indicating predominant grain boundary pinning similar to that obtained for the in situ MgB$_2$ [15, 30]. With the addition of 10 wt.% and 30 wt.% (1.5Mg + 2B), $h_{\text{peak}}$ was changed to 0.35 and 0.24, respectively. For the
30 wt.% added sample, $h_{\text{peak}} \approx 0.24$ suggests that other forms of pinning are active in addition to that from the grain boundaries. However, $h_{\text{peak}}$ increased to 0.36 for the 50 wt.% added sample probably because of excessive addition of (1.5Mg + 2B). For the samples added with 30 wt.% of (1.5Mg + 2B) and sintered at 700 °C, 800 °C, and 1000 °C, the values of $h_{\text{peak}}$ are 0.24, 0.32, and 0.29, respectively. Again, the increase in the $h_{\text{peak}}$ implies that the pinning landscape has changed toward that of normal core.

We now turn to understand more about how $J_c$ is influenced by the pinning mechanism. Looking at Fig. 7a, b, we notice that the sample added with 30 wt.% of (1.5Mg + 2B) ($h_{\text{peak}} \approx 0.24$) and sintered at 700 °C has the weakest field dependency on $J_c$ among others. This could be due to the presence of grain boundary pinning [51] in addition to other forms of pinning in the sample (as reflected in its largest $\Delta T_c$). The absence of grain boundary pinning may also explain the slightly lower in-field $J_c$ of the 50 wt.% added sample ($h_{\text{peak}} \approx 0.36$) than that of the 30 wt.% added one.
Table 3  Onset of critical temperature, \( T_{c-\text{onset}} \), \( T_{c-\text{onset}2} \), offset of critical temperature, \( T_{c-\text{offset}} \) and transition temperature width, \( \Delta T_c \) for ex-situ \( \text{MgB}_2 \) added with different weight percentages of \((1.5\text{Mg} + 2\text{B})\) and sintered at different temperatures

| \( x \) wt.% \((1.5\text{Mg} + 2\text{B})\) | Sintering temperature (\(^\circ\text{C}\)) | \( T_{c-\text{onset}} \) (K) | \( T_{c-\text{onset}2} \) (K) | \( T_{c-\text{offset}} \) (K) | \( \Delta T_c \) (K) |
|---|---|---|---|---|---|
| 0 | 700 | 38.7 | -- | 31.5 | 7.2 |
| 10 | 700 | 38.9 | 30.0 | 23.0 | 15.6 |
| 30 | 700 | 38.6 | 33.0 | 27.6 | 11.2 |
| 50 | 800 | 38.8 | 33.0 | 26.7 | 12.1 |
| 30 | 1000 | 38.8 | 36.0 | 31.6 | 7.2 |

Table 4  Comparison of \( J_c \)'s from this work and some selected previous studies on ex situ and in situ \( \text{MgB}_2 \) added with excess Mg

| Descriptions | Samples and the values of \( J_c \) (A/cm\(^2\)) | References |
|---|---|---|
| Ex situ \( \text{MgB}_2 \) added with \((1.5\text{Mg} + 2\text{B})\) bulk sample \((1000\,^\circ\text{C}, 1\,\text{h})\) | 30 wt.% of \((1.5\text{Mg} + 2\text{B})\) 2.1 \times 10^4 \((0\,\text{T}, 20\,\text{K})\) 3.7 \times 10^3 \((1\,\text{T}, 20\,\text{K})\) 8.0 \times 10^3 \((3\,\text{T}, 20\,\text{K})\) | This work |
| Mixture of 1.1Mg: 2B \((10\,\text{at} \%\, \text{excess Mg})\) to form \( \text{MgB}_2/\text{Fe} \) wires \((750\,^\circ\text{C}, 30\,\text{min})\) | Normal \( \text{MgB}_2 \) wire 3.8 \times 10^3 \((4\,\text{T}, 5\,\text{K})\) 5.4 \times 10^3 \((2\,\text{T}, 20\,\text{K})\) | [45] |
| | 10 at \% excess Mg 13.4 \times 10^3 \((4\,\text{T}, 5\,\text{K})\) 17.5 \times 10^3 \((2\,\text{T}, 20\,\text{K})\) | |
| \( \text{MgB}_2/\text{Fe} \) wires with 10 at \% excess Mg \((600\,^\circ\text{C}, 1\,\text{h})\) | Normal \( \text{MgB}_2 \) wire 2.2 \times 10^4 \((8\,\text{T}, 10\,\text{K})\) 6.3 \times 10^4 \((4\,\text{T}, 20\,\text{K})\) | [40] |
| | 10 at \% excess Mg wire 3.0 \times 10^4 \((8\,\text{T}, 10\,\text{K})\) 7.8 \times 10^4 \((4\,\text{T}, 20\,\text{K})\) | |
| In situ \( \text{MgB}_2 \) powders added with excess Mg | \( \text{Mg:B}=1:2 \) 6.8 \times 10^3 \((10\,\text{kOe}, 20\,\text{K})\) | [31] |
| | \( \text{Mg:B}=1:1 \) 3.4 \times 10^3 \((10\,\text{kOe}, 20\,\text{K})\) |
| | \( \text{Mg:B}=1.5:1 \) 5.9 \times 10^3 \((10\,\text{kOe}, 20\,\text{K})\) |
| In situ \( \text{MgB}_2 \) co-added with 4 wt.\% Ag and excess Mg with composition \( \text{Mg}_x\text{B}_2 \) \( x=1.075\) (\( \text{Mg}_{1.075}\text{B}_2 \)) | Pure sample \( \text{MgB}_2 \) 2.2 \times 10^5 \((0\,\text{T}, 20\,\text{K})\) 3.5 \times 10^5 \((0\,\text{T}, 20\,\text{K})\) 2.4 \times 10^5 \((0.5\,\text{T}, 20\,\text{K})\) 1.4 \times 10^5 \((1\,\text{T}, 20\,\text{K})\) | [46] |

Fig. 6  \( M-H \) hysteresis loop for ex situ \( \text{MgB}_2 \) added for a different weight percentages of \((1.5\text{Mg} + 2\text{B})\) addition and sintered at 700\,^\circ\text{C} \text{for} 1\,\text{h}, \text{b} 30 \text{wt.}\% \((1.5\text{Mg} + 2\text{B})\) added samples sintered at different temperatures for 1 h
For instance, \( J_c \) (20 K) at 1 T and 2 T are 2.1 kA cm\(^{-2}\) and 0.4 kA cm\(^{-2}\), respectively, for the 50 wt.% added sample as compared with 2.5 kA cm\(^{-2}\) and 0.6 kA cm\(^{-2}\), respectively, for the 30 wt.% added sample. Similar phenomenon can also be seen in the 30 wt.% added sample sintered at 700 °C and 800 °C (\( t_{\text{peak}} \approx 0.32 \)) (Fig. 8b). \( J_c \) (20 K) at 1 T and 2 T of the latter are 1.6 kA cm\(^{-2}\) and 0.1 kA cm\(^{-2}\), respectively. For the 30 wt.% added sample sintered at 1000 °C...
(h_{\text{peak}} \approx 0.29), its highest J_c among the samples is attributed to its reinforced grain coupling via solid-state self-sintering [15] as discussed before. Taken all, our results are in agreement with the previous finding that the J_c depends essentially on both the grain coupling and grain boundary pinning strength [51]. Nonetheless, it is a subject of further investigation to elucidate the kinetics of microstructural evolution and its relationship with the pinning mechanism.

4 Conclusion

The role of (1.5Mg + 2B) additions and heat treatment conditions on T_c and J_c of ex situ MgB_2 bulks were investigated in this work. This was done through studying two set of samples: (i) ex situ MgB_2 added with x wt.% (x = 0, 10, 30 and 50) of (1.5Mg + 2B) and sintered at 700 °C for 1 h; (ii) ex situ MgB_2 added with 30 wt.% of (1.5Mg + 2B) and sintered at 700 °C, 800 °C, 1000 °C, respectively, for 1 h. XRD patterns showed the increased fraction of MgB_4 and MgO for the samples sintered at 1000 °C as a result of decomposition of MgB_2. According to the SEM images, the average grain size varied slightly only (0.48–0.56 μm) across the samples. All the samples showed T_{c-onset} \approx 38 K as determined inductively from the measurement of temperature dependence of magnetic susceptibility. A double-step transition of T_c was observed as the amount of the addition was increased. Nonetheless, the width of the double-step transition became narrower with the increasing sintering temperature due to improved MgB_2 phase formation. Self-field J_c at 20 K was increased from 3.0 kA.cm^{-2} to 13.1 kA cm^{-2} upon increasing the addition to 50 wt.%. The J_c was consistently increased to 20.7 kA cm^{-2} as the sintering temperature was raised to 1000 °C. The increment of the J_c is believed to be due to enhanced grain coupling assisted by in situ formation of MgB_2, which filled the voids and connected the MgB_2 grains. As the sintering temperature was increased, solid-state self-sintering took place and resulted in further strengthening of the grain coupling.

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Declarations

Conflict of interest The authors declare no conflict of interest among themselves.

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References

1. J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, Nature 410, 63–64 (2001)
2. Y. Slimani, E. Hannachi, A. Ekicibil, M.A. Almessiere, F.B. Azzouz, J Alloys Compd. 781, 664–673 (2019)
3. M.R. Koblischka, A. Koblischka-Veneva, X. Zeng, E. Hannachi, Y. Slimani, Curr. Comput.-Aided Drug Des. 10, 986 (2020)
4. E. Hannachi, K.A. Mahmoud, Y. Slimani, M.I. Sayyed, Ceram. Int. 48, 24355–24362 (2022)
5. E Hannachi, Y Slimani, M I Sayyed, KA Mahmoud, Ceram. Int. 48, 31902-31908 (2022)
6. M.R. Koblischka, Y. Slimani, M.I. Sayyed, KA Mahmoud, Ceram. Int. 48, 31902-31908 (2022)
7. D.C. Larbalestier, L.D. Cooley, M.O. Rikel, A.A. Polyanskii, J. Magn. Magn. Mater. 27, 414 (2001)
8. D.C. Larbalestier, L.D. Cooley, M.O. Rikel, A.A. Polyanskii, J. Magn. Magn. Mater. 29, 103001 (2008)
9. D.C. Larbalestier, A. Gurevich, D.M. Feldmann, A. Polyanikskii, Nature 414, 368–377 (2001)
10. D. Larbalestier, A. Gurevich, D.M. Feldmann, A. Polyanikskii, Nature 414, 368–377 (2001)
11. M. Muralidhar, M. Higuchi, M. Jirsa, P. Diko, I. Kokal, M. Murakami, IEEE Trans. Appl. Supercond. 27, 6201104 (2017)
12. S.S. Arvapalli, M. Miryala, M. Murakami, J. Supercond. Nov. Magn. 32, 1891–1895 (2019)
13. J.H. Kim, S.X. Dou, J.L. Wang, D.Q. Shi, X. Xu, M.S.A. Hossain, Supercond. Sci. Technol. 20, 448–451 (2007)
14. Z.S. Gao, Y.W. Ma, D.L. Wang, X.P. Zhang, S. Awaaji, K. Watanabe, Chin. Phys. Lett. 27, 3–5 (2010)
15. H. Tanaka, A. Yamamoto, J.I. Shimoyama, H. Ogino, K. Kishio, Supercond. Sci. Technol. 25, 117401 (2012)
16. S. Mizutani, A. Yamamoto, J.I. Shimoyama, H. Ogino, K. Kishio, Supercond. Sci. Technol. 27, 114001 (2014)
17. A. Malagoli, V. Braccini, C. Bernini, G. Romano, M. Vignolo, M. Putti, C. Ferdeghini, Supercond. Sci. Technol. 23, 025032 (2010)
18. M.K. Ben Salem, Y. Slimani, E. Hannachi, A. Hamrita, F.B. Azzouz, M.B. Salem, AIP Conf Proc. 1569, 423–426 (2013)
19. N.M. Hapipii, S.K. Chen, A.S. Halim, M.M.A. Kechik, K.B. Tan, K.P. Lim, O.J. Lee, J. Supercond. Nov. Magn. 32, 1191–1198 (2019)
20. Y. Slimani, M.A. Almessiere, E. Hannachi, M. Mumtaz, A. Manikanad, A. Baykal, F.B. Azzouz, Ceram. Int. 45, 6828–6835 (2019)
21. S.K. Chen, M. Maeda, A. Yamamoto, S.X. Dou, in Vortices and nanostructured superconductors, ed. by A. Crisan, Ed. Switzerland (Springer Series in Materials Science, Switzerland, 2017), pp.65–108
22. W.X. Li, R. Zeng, J.L. Wang, Y. Li, S.X. Dou, J. Appl. Phys. 111, 07E135 (2012)
23. A.V. Pan, S. Zhou, H. Liu, S. Dou, Supercond. Sci. Technol. 16, 639–644 (2003)
24. P. Kovač, M. Reissner, T. Melišek, I. Hušek, S. Mohammad, J. Appl. Phys. 106, 013910 (2009)
25. D.X. Chen, R.B. Goldfarb, J. Appl. Phys. 66, 2489–2500 (1989)
26. M. Miryala, S.S. Arvapalli, P. Diko, M. Jirsa, M. Murakami, Adv. Eng. Mater. 22, 1900750 (2020)
27. P. Kovač, I. Hušek, T. Melišek, J.C. Grivel, V. Pachala, V. Štríbew, R. Didusko, J. Homeyer, N.H. Andersen, Supercond. Sci. Technol. 17, L41–L46 (2004)
28. J.H. Kim, S.X. Dou, D.Q. Shi, M. Rindfleisch, M. Tomsic, Supercond. Sci. Technol. 20, 1026–1031 (2007)
29. K.Y. Tan, K.L. Tan, K.B. Tan, K.P. Lim, S.A. Halim, S.K. Chen, J. Supercond. Nov. Magn. 24, 2025–2029 (2011)
30. N.M. Hapipii, M. Miryala, S.K. Chen, S.S. Arvapalli, M. Murakami, M.M.A. Kechik, K.B. Tan, O.J. Lee, Ceram. Int. 46, 23041–23048 (2020)
31. B.B. Sinha, M.B. Kadam, M. Mudgel, V.P.S. Awana, H. Kishan, S.H. Pawar, Physica. C 470, 25–30 (2010)
32. Y. Guo, W. Zhang, D. Yang, R. Yao, J. Am. Ceram. Soc. 95, 754–759 (2012)
33. S. Bruttì, A. Ciccioli, G. Balducci, G. Gigli, P. Manfrinetti, A. Palenzona, Appl. Phys. Lett. 80, 2892–2894 (2002)
34. G.A.B. Matthews, S. Santra, R. Ma, C.R.M. Grovenor, P.S. Grant, S.C. Speller, Supercond. Sci. Technol. 33, 1–23 (2020)
35. G. Balducci, S. Bruttì, A. Ciccioli, G. Gigli, P. Manfrinetti, A. Palenzona, M.F. Butman, L. Kudin, J. Phys. Chem. Solids 66, 292–297 (2005)
36. D.G. Hinks, J.D. Jorgensen, H. Zheng, S. Short, Physica. C 382, 166–176 (2002)
37. M. Shahabuddin, N.S. Alzayed, S. Oh, S. Choi, M. Maeda, S. Hata, Y. Shimada, M.A.S. Hossain, J.H. Kim, AIP Adv. 4, 017113 (2014)
38. E.W. Collings, M.D. Sumption, M. Bhatia, M.A. Susner, S.D. Bohnenstein, Supercond. Sci. Technol. 21, 103001 (2008)
39. H. Zhang, L. Li, Y. Zhao, Y. Zhang, J. Phys. Cond. Mat. 26, 012057 (2014)
40. R. Zeng, L. Lu, W.X. Li, J.L. Wang, D.Q. Shi, J. Horvat, S.X. Dou, M. Bhatia, M. Sumption, E.W. Collings, J.M. Yoo, M. Tomsic, M. Rindfleisch, J. Appl. Phys. 103, 083911 (2008)
41. H. Zhang, Y. Zhao, Y. Zhang, J. Supercond. Nov. Magn. 28, 2711–2714 (2015)
42. F. Wu, J. Low Temp. Phys. 177, 157–164 (2014)
43. S.K. Chen, A. Serquis, G. Serrano, K.A. Yates, M.G. Blamire, D. Guthrie, J. Cooper, H. Wang, S. Margadonna, J.L. MacManus-Driscoll, Adv. Funct. Mater. 18, 113–120 (2008)
44. I. Kortus, O.V. Dolgov, R.K. Kremer, A.A. Golubov, Phys. Rev. Lett. 94, 027002 (2005)
45. R. Zeng, L. Lu, J.L. Wang, J. Horvat, W.X. Li, D.Q. Shi, S.X. Dou, M. Tomsic, M. Rindfleisch, Supercond. Sci. Technol. 20, L43–L47 (2007)
46. S.S. Arvapalli, M. Miryala, M. Murakami, Adv. Eng. Mater. 21, 1900497 (2019)
47. M. Eisterer, Phys. Rev. B 77, 144524 (2008)
48. M. Muralidhar, N. Kenta, M.R. Kobliuschka, M. Murakami, Phys. Status Solidi Appl. Mater. Sci. 212, 2141–2145 (2015)
49. D. Dew-Hughes, Philos. Mag. 30, 293–305 (1974)
50. W. Pachla, A. Presz, R. Diduszko, P. Kovác, I. Husek, Supercond. Sci. Technol. 15, 1281–1287 (2002)
51. M. Teruo Matsushita, A.Y. Kiuchi, J. Shimoyama, K. Kishio, Supercond Sci. Technol. 21, 015008 (2008)

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