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Enhanced critical current density of *in situ* processed MgB_2 bulk superconductors with MgB_4 additions

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Abstract

The effects of MgB_4 addition on the superconducting properties and the microstructure of *in situ* processed MgB_2 bulk superconductors were studied. MgB_4 powder of 1-20 wt.% was mixed with (Mg + 2B) powder and then pressed into pellets. The pellets of (Mg + 2B + xMgB_4) were heat-treated at 650 ℃ for 1 h in flowing argon. The powder X-ray diffraction (XRD) analysis for the heat-treated samples showed that the major formed phase in all samples was MgB_2 and the minor phases were MgB_4 and MgO. The full width at half maximum (FWHM) values showed that the grain size of MgB_2 decreased as the amount of MgB_4 addition increased. MgB_4 particles included in a MgB_2 matrix is considered to suppress the grain growth of MgB_2. The onset temperatures ($T_{c,onset}$) of MgB_2 with MgB_4 addition (0-10 wt.%) was between 37-38 K. The 20 wt.% MgB_4 addition slightly reduced the $T_{c,onset}$ of MgB_2 to 36.5 K. This result indicates that MgB_4 addition did not influence the superconducting transition temperature (T_c) of MgB_2 significantly. On the other hand, the small additions of 1-5 wt.% MgB_4 increased the critical current density (J_c) of MgB_2. The J_c enhancement by MgB_4 addition is attributed not only to the grain size refinement but also to the possible flux pinning of MgB_4 particles dispersed in a MgB_2 matrix.

Keywords : MgB_2, MgB_4 addition, Superconductor, Critical current density (J_c), Grain refinement

1. INTRODUCTION

A MgB_2 superconductor has a high superconducting critical temperature (T_c) of 39 K [1] and a high critical current density (J_c) at magnetic fields [2]. In addition to the excellent superconducting properties, other merits of MgB_2 are its long coherent length [3] and the small current anisotropy [4-5]. Moreover, the raw materials (Mg and B) of MgB_2 are not expensive and easy to obtain. Owing to these merits, MgB_2 is believed to be a promising material that can replace a conventional NbTi superconductor. A superconducting magnetic designed using MgB_2 superconducting wires can be operated at 20 K using an electrical cooler instead of liquid helium.

For practical applications of a MgB_2 superconductor the J_c under magnetic fields should be enhanced. The presence of defects in superconducting grains or at the grain boundaries of MgB_2 leads to the J_c enhancement of MgB_2. The defects can be made artificially either through physical [6-13] or chemical [14-16] methods. Particle (neutron, electron or ion) irradiation is a well-known process that can form defects physically through the collision of accelerated particles to the targeting materials. Small defects such as vacancies and cavities can be formed in the superconducting matrix through particle irradiation [15-20]. As a result of the defect formation, the J_c at the magnetic fields of the particle-irradiated MgB_2 was much higher than that of MgB_2 with no irradiation [21,22]. Along with the physical method, the J_c of MgB_2 can be increased by the doping of chemical species such as silicon carbide [23], carbon-related materials [24], and other fine impurity phases [25]. The carbon doping to MgB_2 not only led to the formation of a lattice strain [26], and lattice substitution [26-31] but also increased the number of grain boundaries [32]. Mechanical milling for boron powder is an alternative way to increase the J_c of MgB_2 through the grain size refinement of MgB_2 [32].

In this experiment, MgB_4 powder was synthesized using Mg and B powder by the powder reaction process. MgB_4 is a phase that is compatible with MgB_2 in a Mg-B binary phase diagram. MgB_4 is often formed with MgB_2 in the powder reaction process using boron-enriched compositions. The synthesized MgB_4 powder was used as an additive of *in situ* processed MgB_2 bulk superconductors. The added amount of MgB_4 was changed from 0 to 20 wt.%. The effects of MgB_4 addition on the J_c, T_c and the microstructure of MgB_2 were investigated.

2. EXPERIMENTAL PROCEDURE

MgB_4 powder used as an additive for MgB_2 superconductors was synthesized by the powder reaction method of (Mg + 4B = MgB_4) using Mg and B powders.

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The detailed preparation condition of MgB_4 was well described in previous reports [33-38]. The impurity phases included in the synthesized MgB_4 powder were removed by the HNO_3 leaching process [36].

MgB_2 bulk superconductors were fabricated through an *in situ* reaction process using Mg and B powders. Mg and B powders with a ratio of Mg:B=1:2 were mixed for 30 min by hand mixing using a mortar jar and pestle. To compensate the possible Mg loss during heat treatment, 10 wt.% of Mg was intentionally added to a mixture of (Mg + 2B). MgB_4 powder of 1-20 wt.% was added to the mixture of (Mg + 2B) powder.

0.3 g of a powder mixture of (Mg + 2B + x wt.% MgB_4) was put in a steel mold with a diameter of 10 mm and was uniaxially pressed into a pellet. The pressed pellet was encapsulated with a Ti tube to suppress the possible oxidation of Mg during heat treatment. To determine out the optimum heat treatment condition for the formation of MgB_2, the heat treatment temperature and time were varied. We determined the heat treatment temperature as 650℃, which is a temperature just above a melting point of Mg and the heat treatment period as 1 h. The short period of 1 h at 650℃ is to minimize the grain growth of MgB_2. The Ti-encapsulated pellets were located at the center of a tubular furnace, heated to 650℃ at a rate of 100℃/h in flowing argon gas, maintained for 1 h and then cooled to room temperature in a furnace.

The heat treated pellets were crushed into a powder form for a phase analysis. The formed phases after heat treatment were analyzed using an X-ray diffraction method (XRD) for the power samples. From the peak intensity of each phase in XRD patterns, volume fractions of the formed phases and the second residual phases were calculated using eq. (1).

$$F(MgB_2) = \frac{\sum I_{MgB_2}}{\sum I_{MgB_2} + \sum I_{MgB_4} + \sum I_{MgO}} \quad (1)$$

where F(MgB_2) is a volume fraction of MgB_2, and I_{MgB2} and I_{MgB4} and I_{MgO} are the peak intensities of MgB_2, MgB_4 and MgO, respectively.

To measure T_c and J_c of MgB_2 bulk superconductors, rectangular specimens with approximate dimensions of 3×3×2 mm were cut from the heat-treated pellets using a diamond saw. Susceptibility-temperature curves (*M-T*) and magnetization-magnetic field (*M-H*) curves are obtained using a magnetic properties measurement system (MPMS) with a maximum magnetic field of 5 Tesla. J_c at 5 K and 20 K was calculated using the extended Bean's critical model [39] of eq. (2).

$$J_c = 20\Delta M/a(1-a/3b) \quad (2)$$

where ΔM is the magnetization difference (M_decreasing field region-M increasing field region) in a constant magnetic field, and *a* and *b* are parameters regarding the sample dimension.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the samples with (0-20 wt.%) MgB_4 additions, heat-treated at 650℃ for 1 h. The major formed phase of all samples is MgB_2 regardless of the amount of MgB_4 additions. The addition of MgB_4 appears to not affect the formation of MgB_2. As the amount of MgB_4 addition increases, the peaks of MgB_4 are intensified (see the XRD patterns with 10 and 20 wt.% MgB_4 additions). Another minor phase formed in the heat-treated pellets is MgO. Small MgO peaks observed in all XRD patterns are attributed to the oxidation of Mg during heat treatment.

According to the XRD results of Fig. 1, the formation reaction of MgB_4 at the give heat treatment condition can be described by eq. (3).

$$Mg + 2B + xMgB_4 = MgB_2 + xMgB_4 + yMgO \quad (3)$$

At the heat treatment temperature of 650℃, MgB_2 forms through the liquid phase reaction between a Mg melt and a solid B powder, because the heat treatment temperature is high than m. p. (649℃) of Mg. The formation reaction of MgB_2 would be conducted by the mass transfer through the Mg melt. Most of the Mg is thought to be consumed to form MgB_2 through the reactions of (Mg + 2B = MgB_2) and (MgB_4 + Mg = MgB_2). Some of the Mg might be consumed for the oxidation of Mg or be evaporated during heat treatment. Because 10 wt.% of Mg was intentionally added to the raw powders of (Mg + B) to compensate the Mg loss, the amount of Mg was sufficient for the formation reaction of MgB_2. In the case of large MgB_4 additions, The peaks of MgB_4 were present together with MgB_2. The MgB_4 is supposed to be present as a discrete particle form within MgB_2 grains or at the grain boundaries of MgB_2.

Fig. 2 shows the volume fraction of the formed phases in the samples with MgB_4 additions, calculated using eq. (1).

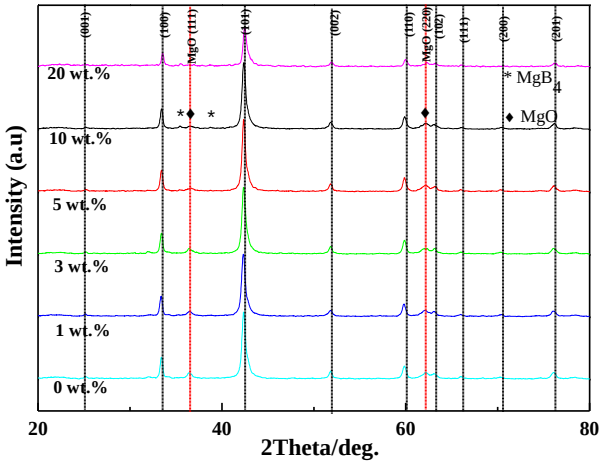

Fig. 1. XRD patterns of the samples with MgB_4 additions, heat-treated at 650℃ for 1 h.

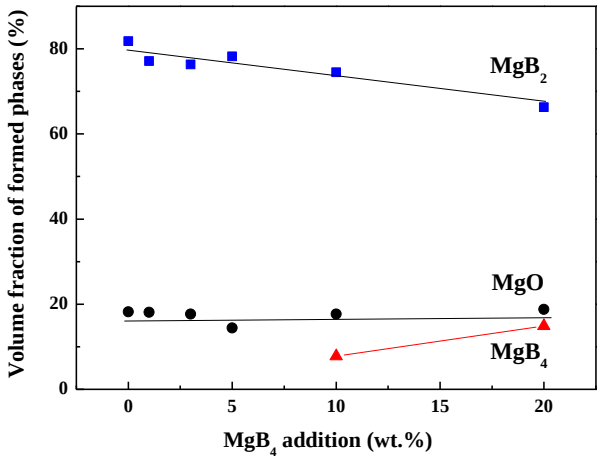

Fig. 2. Volume fractions of MgB_2, MgB_4 and MgO as a function of the amount of MgB_4 addition.

TABLE I
LATTICE PARAMERS AND FWHM VS. AMOUNT OF MgB_4 ADDITION.

Amount of MgB_4 (wt.%)	FWHM (deg.)		Lattice parameter (Å)	
	(110)	(002)	a	c
0	0.389	0.443	3.090	3.532
1	0.415	0.449	3.091	3.500
3	0.405	0.413	3.087	3.534
5	0.391	0.425	3.088	3.540
10	0.403	0.455	3.090	3.526
20	0.396	0.486	3.087	3.497

The volume fraction of MgB_2 of the sample with no addition is approximately 80%. As is normally expected, the volume fraction of MgB_2 is dependent on the added amount of MgB_4. The volume fractions of MgB_2 for the sample with 10 wt.% and 20 wt.% MgB_4 additions are 74% and 66.3%, respectively. Interestingly, the volume fraction of the MgO formed during heat treatment is approximately 18% regardless of the MgB_4 addition.

Through a precise analysis of the XRD patterns of Fig. 1, the lattice parameters of MgB_2 and the full width at half maximum (FWHM) of the peaks were calculated, the results of which are summarized in TABLE I. As illustrated in TABLE I, the lattice parameters *a* and *c* were not influenced by the MgB_4 additions. This is because both MgB_2 and MgB_4 are stoichiometric line compounds and there is no interaction between MgB_2 and MgB_4 (MgB_4 is a high temperature phase). The values of FWHM estimated from the (110) and (002) peaks of MgB_2 increase as the amount of MgB_4 addition increases, which indicates the change in the grain size of MgB_2.

The grain sizes of MgB_2 samples with no addition and MgB_4 additions were calculated from the formula $t= 0.9\lambda/BCOS\theta$ [40] using the FWHM data. Where t is the grain (crystallite) size, λ is the wavelength of the target used, B is the half width of the peak, and θ is the Bragg angle of the incident beam.

Fig. 3 shows the variation of the grain size of MgB_2 as a function of the amount of MgB_4 addition. The grain size of

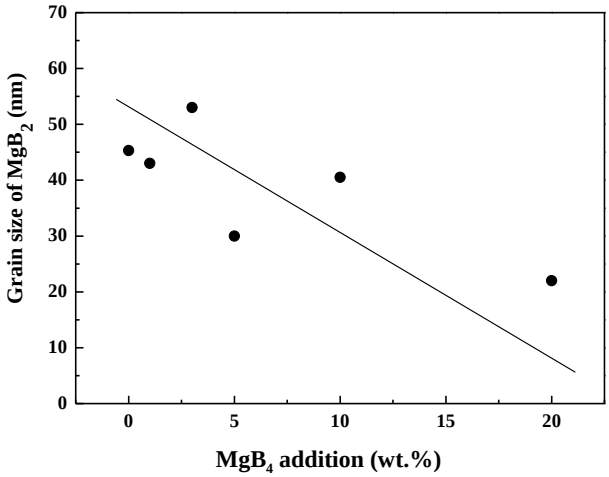

Fig. 3. Variation of grain size of MgB_2 as a function of the amount of MgB_4 addition.

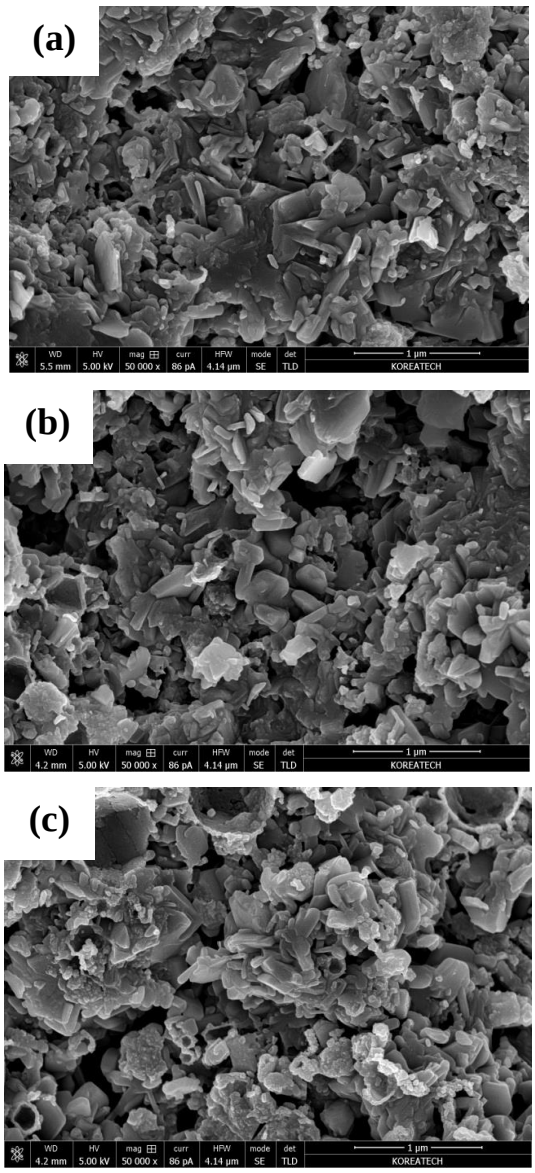

Fig. 4. SEM micrographs of samples with (a) no addition, (b) 5 wt.% MgB_4 addition, and (c) 20 wt.% MgB_4 addition.

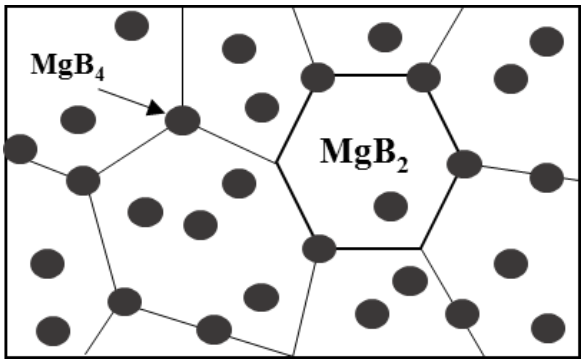

Fig. 5. Schematics of dispersed MgB_4 particles in an MgB_2 grain structure.

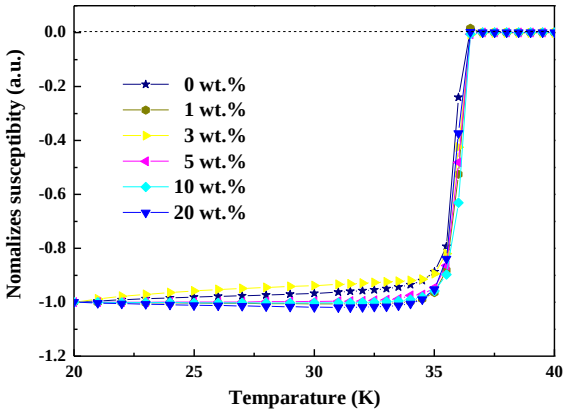

Fig. 6. Normalized susceptibility-temperature curves of the samples with MgB_4 additions.

MgB_2 with no addition is 45 nm. The grain size decreases as the amount of MgB_4 addition increases. For 5 wt.% and 20 wt.% MgB_4 additions, the grain sizes of MgB_2 are 30 nm and 22 nm, respectively. These results indicate that the MgB_4 addition suppressed the grain growth of MgB_2. In other words, a larger grain boundary area exists in the pellet with MgB_4 addition in comparison with no addition.

Fig. 4 shows SEM micrographs of the samples with (a) no addition, (b) 5 wt.% MgB_4 addition and (c) 20 wt.% MgB_4 addition. Many plate-like grains whose thickness is smaller than 1 μm are observed in sample (a). As already confirmed through the XRD analysis of Fig. 1, approximately 80 % of the formed phase of sample (a) was MgB_2. It can thus be said that the plate-like grains are MgB_2. The SEM investigation showed that the grain size of MgB_2 decreased as the amount of MgB_4 addition increased The MgB_2 grains observed in the sample with 20 wt. % MgB_4 addition are smaller than that of sample (a) (see Fig. 4c)). The SEM observation agrees with the XRD FWHM of Fig. 2.

The reason why the grain growth of MgB_2 was suppressed by the addition of MgB_4 can be explained in terms of the thermal stability of MgB_4 at the heat treatment temperatures. There is a large difference in the melting temperature between Mg and B. The m. p. of B is as high as 2300℃ [41], whereas the m. p. of Mg is very low at 649℃ [42]. MgB_4, which has more boron than MgB_2, would be more stable at high temperature. The MgB_4 particles can be present at the grain boundaries of MgB_2 or trapped within MgB_2 grains (see the schematic illustration in Fig. 5). The MgB_4 particle present at the grain boundaries of MgB_2 can suppress the grain growth of MgB_2 during heat treatment.

Fig. 6 shows normalized susceptibility-temperature (*M*-*T*) curves of the samples with various MgB_4 additions. $T_{c,onset}$ and $T_{c,mid}$ of the sample with no addition are 37 K and 35.9 K, respectively, whereas $T_{c,onset}$ and $T_{c,mid}$ of the sample with 10 wt.% MgB_4 addition are 37 K and 36.1 K, respectively. In the case of a large MgB_4 addition of 20 wt.%, $T_{c,onset}$ and $T_{c,mid}$ are 36.5 K and 35.8 K, which are slightly lower than the other samples. The superconducting critical temperatures seem to not be significantly influenced by the MgB_4 addition. The *M*-*T* result confirms again that MgB_4 is a chemically stable and thermally compatible additive with MgB_2, which does not react with a superconducting MgB_2. The superconducting critical temperatures of the samples with various MgB_4 additions are summarized in TABLE II.

TABLE II
SUPERCONDUCTING TRANSITION TEMPERATURES OF THE SAMPLES WITH MgB_4 ADDITIONS.

MgB_4 addition (wt.%)	Superconducting critical temperatures of MgB_2 (K)	
	$T_{c,onset}$	$T_{c,mid}$
0	37	35.9
1	37	36.0
3	37.5	36.3
5	38	37.3
10	37	36.1
20	36.5	35.8

Fig. 7 shows J_c-*B* curves at 5 K and 20 K of samples with MgB_4 additions, heat-treated at 650℃ for 1 h. The J_cs at 5 K of the samples with 1-5 wt.% MgB_4 additions are slightly higher than that of the sample with no addition. Moreover, J_c at 5 K of the sample with 10 wt.% MgB_4 is similar to that of the sample with no addition, in spite of the low volume fraction of MgB_2. The enhanced J_c of the samples with small MgB_4 additions is attributed to the grain refinement and the presence of MgB_4 particles in the superconducting MgB_2 matrix, which were already observed by FWHM and SEM investigations (Figs. 3 and 4). These two factors appear to act as flux pinning centers which pin the magnetic flux. When the amount of MgB_2 addition is more than 20 wt.%, J_c decreases because the superconducting volume fraction in the sample decreases. Although not shown here, in our study, the addition of MgB_4 up to 70% resulted in a decrease in J_c in proportion to the amount added.The J_c-B characteristics at 20 K of samples with MgB_4 additions shows similar trend to that at 5 K: 1-5 wt.% MgB_4 additions increases the J_c of MgB_2.

Fig. 8 shows the J_c-*B* curves at 5 K and the magnetic fields of 3.5-5.0 T. With the exception of the 20 wt.% MgB_4 addition, the J_c values at 5 K and the given applied magnetic fields of the samples are higher than that of the sample with no addition. J_c at 5 K, 4 T of the sample with no addition is 50,850 A/cm^2, whereas J_cs at 5 K, 4 T of the samples with 1 wt.% and 3 wt.% MgB_4 adidtions are 59,920 A/cm^2 and 60,760 A/cm^2, respectively.

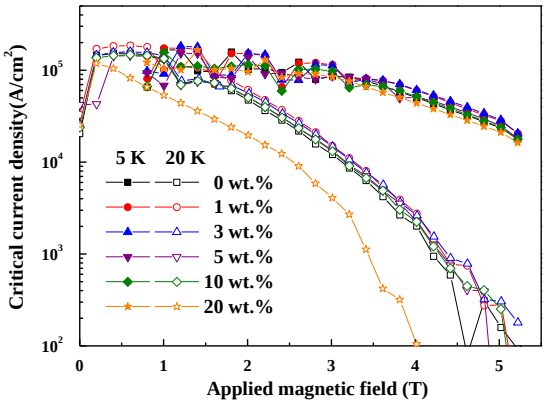

Fig. 7. J_c-B curves at 5 K and 20 K of the samples with 0-20 wt.% MgB_4 additions.

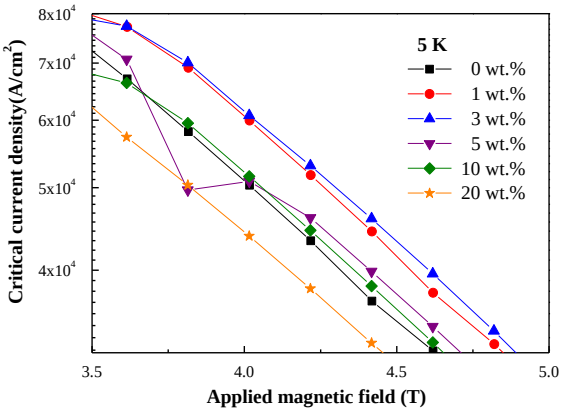

Fig. 8. J_c-B curves at 5 K and magnetic fields of 3.5 T-5.0 T of the samples with 0-20 wt.% MgB_4 additions.

4. CONCLUSIONS

We studied the effects of MgB_4 additions (1-20 wt.%) on the superconducting properties of MgB_2 bulk superconductors prepared using the powder reaction process. The onset temperature ($T_{c,onset}$) of MgB_2 with MgB_4 addition (0-10 wt.%) was between 37-38 K. Even for a large MgB_4 addition of 20 wt.%, the $T_{c,onset}$ was 36.5 K. This result indicates that the MgB_4 addition did not significantly influence the superconducting transition temperature (T_c) of MgB_2. On the other hand, the small MgB_4 additions of 1-5 wt.% increased the critical current density (J_c) of MgB_2. Moreover, the J_c level of MgB_2 with 10 wt.% MgB_4 addition was similar to that of MgB_2 with no addition in spite of the reduced superconducting volume. The FWHM and SEM investigation showed that the grain size of MgB_2 decreased as the amount of MgB_4 addition increased. The presence of MgB_4 in a MgB_2 matrix is likely to suppress the grain growth of MgB_2 at the heat treatment temperature. The J_c enhancement of MgB_2 by the MgB_4 addition appears to be attributed to the grain size refinement of MgB_2 and the possible flux pinning of MgB_4 particles dispersed within MgB_2 grains.

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