pISSN 1229-3008 eISSN 2287-6251
Progress in Superconductivity and Cryogenics
Vol.19, No.1, (2017), pp.42~46 https://doi.org/10.9714/psac.2017.19.1.042

Effects of heat treatment temperature on the formation of MgB_2 bulk superconductors prepared using MgB_4 and Mg powder

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(Received 26 January 2017; revised or reviewed 20 February 2017; accepted 21 February 2017)

Abstract

The effects of the heat treatment temperature (600℃-1050℃) on the formation of MgB_2 and the superconducting properties have been examined. The self-synthesized MgB_4 and commercial Mg powders were used as raw materials for the formation of MgB_2. The superconducting critical temperatures (T_cs) of MgB_2 bulk superconductors prepared at 600℃-850℃ were as high as 37-38 K regardless of the heat treatment temperature. However, because MgB_4 is more stable than MgB_2 at above 850℃, no superconducting signals were detected in the susceptibility-temperature curves of the samples prepared above 850℃. As for the critical current density (J_c), the sample heat-treated at a low temperature (600℃) for a prolonged period (40 h) showed a J_c higher than those prepared at 650℃-850℃ for a short period (1 h). The FWHM (full width at half maximum) result showed that the grain size of MgB_2 of the 600℃ sample was smaller than that of the other samples. The high J_c of the 600℃ sample is attributed to the presence of large numbers of grain boundaries, which can act as flux pinning centers of MgB_2.

Keywords : MgB_4, MgB_2, Critical current density (J_c), Powder reaction, Phase formation, Heat treatment temperature

1. INTRODUCTION

The superconducting critical temperature (T_c) of MgB_2 is 39 K, which is the highest value among intermetallic low-temperature superconductors [1]. In addition to the high T_c, the low current anisotropy and long coherence length are other merits of MgB_2 [2]. However, a low sintering density [3], poor mechanical strength, and flux creep [4] are problems to be solved for the practical applications of MgB_2.

The properties of MgB_2 are dependent not only on the fabrication processing but also on the precursor materials used. There are two different methods that can be used to fabricate MgB_2: an *ex-situ* process [5-8] and an *in-situ* [9-12]. In the *ex-situ* process MgB_2 powder was used as a precursor [5-8]. Although the sintering density of the *ex situ* processed MgB_2 was high, the critical current density (J_c) was very low. This is because of the weakly-linked grain boundaries of MgB_2 [5]. On the other hand, with the *in-situ* process, a mixture of Mg and B powders were used as raw materials [9-12]. The *in situ* processed MgB_2 showed a J_c higher than that of the *ex-situ* processed MgB_2. This is attributed to the high flux pinning capability caused by the strongly coupled grain boundaries [13] and lattice strain [14]. The *in situ* processed MgB_2, however, showed a low sintering density. Many pores, which are a byproduct of the formation reaction of MgB_2, were included in the microstructure of the *in situ* processed MgB_2 [9,10]. If the porosity of the *in situ* processed MgB_2 is reduced, the J_c is expected to increase further.

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Recently, a new fabrication process, which can synthesize MgB_2 through a reaction between MgB_4 and Mg has been developed [16-21]. In this process, instead of Mg and B powders, MgB_4 and Mg powders are used as raw materials to increase the sintered density of MgB_2. A relatively smaller amount of Mg (one half of the *in situ* process) is used to form the same molar fraction of MgB_2, in comparison with the convention *in situ* process using 2Mg and 4B powder [21]. Because the pores are developed by the melting of Mg powders during heat treatment, consequently, the number of pores developed in the new process was smaller [15].

In this study the effects of the heat treatment temperature on the formation of MgB_2 bulk superconductors prepared using MgB_4 and Mg powders was studied. The formation of MgB_2 and the microstructures developed at each reaction temperature were examined. Superconducting properties (T_c and the J_c) of the prepared MgB_2 samples were also measured.

2. EXPERIMENTAL PROCEDURE

Mg (99.6% purity, average size 4-6 ㎛, spherical in shape) and B (95-97%, average size 1㎛) powders were used as raw materials to synthesize MgB_4. The powders were weighed to a ratio of Mg:B=1:4 and mixed by hand mixing using a pestle and mortar. The mixed powder was put in a steel mold with a diameter of 30 mm and pressed into a pellet. The pellet was encapsulated using a Ti tube to prevent the possible oxidation of Mg during heat treatment.

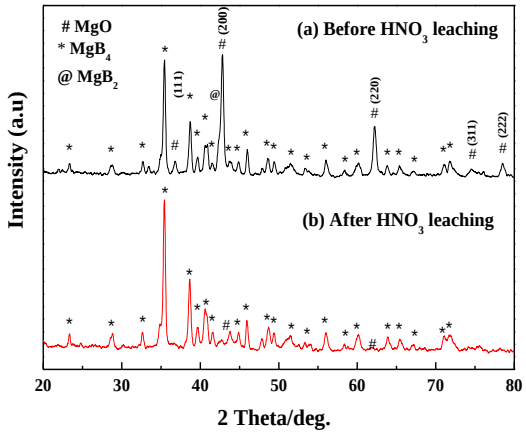

Fig.1. Powder X-ray diffraction patterns of a heat-treated pellet heat-treated at 1000℃ for 5 h: (a) before and (b) after HNO_3 leaching.

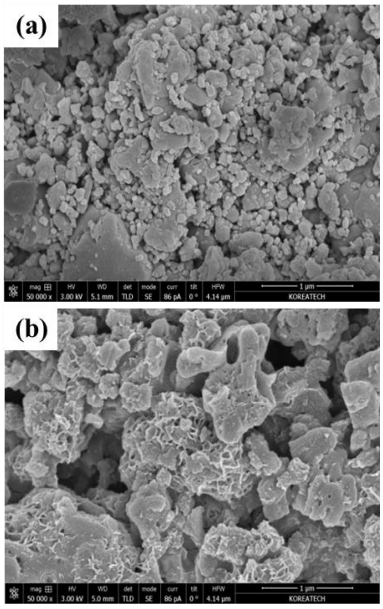

Fig. 2. SEM micrographs of the heat-treated pellets at 1000℃ for 5 h: (a) before and (b) after HNO_3 leaching.

The Ti-encapsulated pellets were located at the center of a tubular furnace and heat-treated at 1000℃ for 5 h in flowing argon gas. After the heat treatment, the pellets were taken out of the Ti tube and crushed into a power form.

The formed phase in the heat-treated pellet was analyzed using an X-ray diffraction method (XRD). According to the XRD analysis for the heat-treated pellets, a major formed phase of MgB_4 and undesirable second phases such as MgO and MgB_2, which formed the oxidation of Mg and the low-temperature formation reaction of MgB_2 during heating, were also present (see Fig. 1(a)). To remove the undesirable phases, the crushed powders were put in a 1 mole HNO_3 solution and stirred magnetically for 1 h. The detailed procedure of the HNO_3 leaching process was well described in the literature [19]. It was confirmed in our experiment that most of the MgO and MgB_2 was dissolved completely in the HNO_3 solution, and a high purity MgB_4 powder was obtained (Fig. 1(b)).

Fig. 2 shows scanning electron micrographs (SEM) of the synthesized powders: (a) before and (b) after HNO_3 leaching. Many granular particles, which are considered MgB_4, MgB_2, or MgO particles, are present in sample (a). The size of the formed particles is smaller than 1 μm. After the HNO_3 leaching process, a network structure formed on the surface of the particle agglomerates owing to the dissolution of MgO and MgB_2 in the HNO_3 solution (see sample (b)).

MgB_2 bulk superconductors were made using the synthesized MgB_4 and commercial Mg powder with an average size of 25 μm. The two raw powders were mixed for 30 min by hand mixing using a mortar jar and pestle. 0.3 g of the powder mixture of ($Mg+MgB_4$) were put in a steel mold with a diameter of 10 mm and uniaxially pressed into a pellet. Some pellets were heat-treated at 600℃ for a prolonged period of 40 h, and others were heat-treated at 650℃-1050℃ for a short period of 1 h in flowing argon gas. Because a melting temperature of Mg is 650℃, the formation reaction of MgB_2 below 650℃ will be slowly achieved through a solid state reaction by eq. (1-1), whereas the formation reaction above 650℃ will rapidly be achieved through the liquid state reaction according to eq. (1-2).

$$\text{Below } 650℃: MgB_4 + Mg\ (solid) = 2MgB_2 \quad (1\text{-}1)$$

$$\text{Above } 650℃: MgB_4 + Mg\ (liquid) = 2MgB_2 \quad (1\text{-}2)$$

To measure T_c and J_c of MgB_2 bulk samples, rectangular specimens with an approximate dimension of 3×3×2 mm were taken from the heat-treated pellets using a diamond saw. Magnetization-temperature (*M-T*) curves and magnetization-magnetic field (*M-H*) curves are measured using a magnetic property measurement system (MPMS) with a maximum magnetic field of 5 Tesla. The J_c at 5 K and 20 K were calculated using an extended Bean's critical model [22] of eq. (2)

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

where ΔM is the magnetization difference (M_decreasing field region-M_increasing field region) at a constant magnetic field, and *a* and *b* are parameters regarding the sample dimensions.

3. RESULTS AND DISCUSSION

Fig. 3 shows the powder XRD patterns of samples prepared at 600℃-1050℃. The major formed phase of samples prepared at 600℃ for 40 h and at 650℃-850℃ for 1 h are MgB_2, whereas a major formed phase above 860℃ is MgB_4. This is because MgB_4 is a stable phase at a high temperature. In addition to the presence of MgB_4, MgO formed in all pellets, although the pellets were encapsulated with a Ti tube to suppress the oxidation of Mg. The presence of MgO is attributed to the high reactivity of Mg powder, which is easy to react with oxygen included in argon gas.

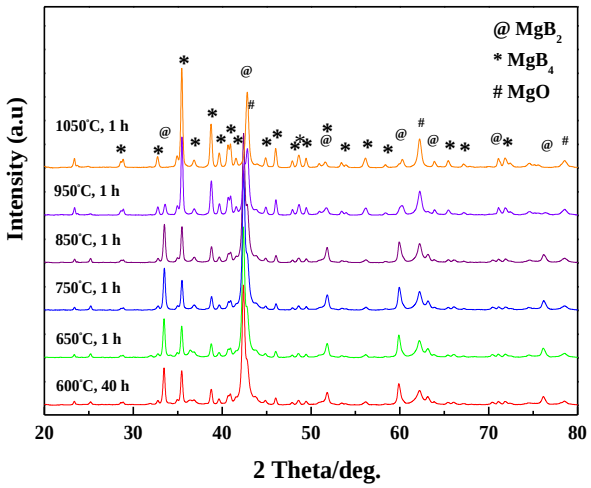

Fig. 3. Powder X-ray diffraction patterns of the samples prepared under various heat treatment conditions.

The volume fraction of MgB_2 of the prepared samples is qualitatively analyzed from the peak intensity of MgB_2 in the XRD patterns. The peak intensity level of MgB_2 of the samples heat-treated at 650℃-850℃ for 1 h is almost the same as that of the sample heat-treated at 600℃ for 40 h. This indicates that the formation reaction of MgB_2 in a liquid state was faster than that in a solid state owing to the fast mass transfer through the Mg melt.

The lattice parameters, *a* and *c* and FWHM are calculated from data of the XRD patterns of Fig. 3, the results of which are summarized in TABLE 1. There were no significant differences in lattice parameters *a* and *c* of MgB_2 among the samples prepared at 600℃-850℃, whereas there exists a difference in the full width at half maximum (FWHM) among the samples. The values of FWHM increases as the heat treatment temperature increases, which indicates the increase of a grain size of MgB_2.

The grain size (crystallite size) of MgB_2 was calculated from eq. (3) [23] using the data of FWHM of XRD peaks.

$$t = 0.9\lambda/B\cos\theta \quad (3)$$

where t is the grain size, λ is the wavelength of the target used, B is the half width of a peak and θ is the angle of an incident beam.

Fig. 4 shows grain size of MgB_2 as a function of heat treatment temperature. As can be seen in the figure, the grain size of MgB_2 increases as the heat treatment temperature increases. The grain size of MgB_2 heat-treated at 600℃ for 40 h is 70 nm, whereas the grain sizes of MgB_2 heat-treated at 650℃, 750℃, 850℃ and 950℃ for the same period of 1 h are 81 nm, 90 nm, 108 nm, and 128 nm, respectively. The heat treatment above the m. p. of Mg leads to a significant grain growth of MgB_2, as well as the accelerated formation reaction of MgB_2 [13].

TABLE 1.
LATTICE PARAMETERS *a* AND *c*, AND FULL WIDTH HALF MAXIMUM OF MgB_2 HEAT-TREATED AT VARIOUS TEMPERATURES.

Heat treatment condition	Parameter a (Å)	Parameter c (Å)	FWHM
600℃, 40 h	3.0891	3.5263	0.264
650℃, 1 h	3.0872	3.5288	0.258
750℃, 1 h	3.0872	3.5244	0.268
850℃, 1 h	3.0858	3.5251	0.269
950℃, 1 h	3.0687	3.5314	0.331
1050℃, 1 h			0.337

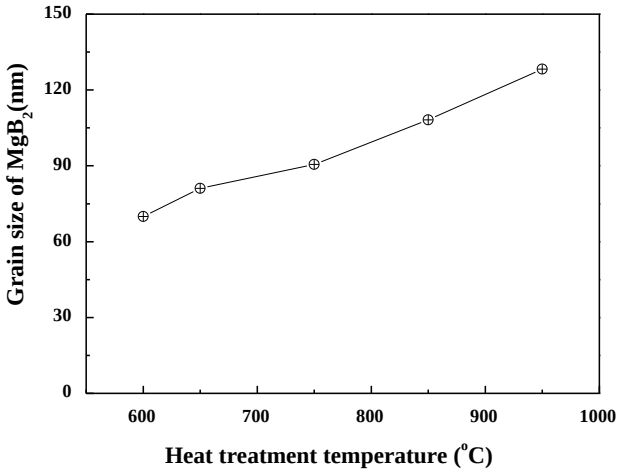

Fig. 4. Grain size of MgB_2 as a function of heat treatment temperature.

Fig. 5 shows SEM micrographs of the samples heat-treated at (a) 650℃ for 1 h, (b) 750℃ for 1 h, and (c) 850℃ for 1 h. Many plate-like grains with a size smaller than 1 μm are observed in sample (a). According to the XRD analysis of Fig. 3, a major phase of sample (a) was MgB_2. It is, therefore, reasonable that the plate-like grains of sample (a) are considered as MgB_2. The size of the plate-like grains of samples (b) and (c) seem to be larger than that of sample (a). This result agrees with the results of the FWHM data of Fig.4.

Fig. 6 shows *M*-*T* curves of the samples heat-treated at 600℃ for 40 h, 650℃ for 1 h, 750℃ for 1 h and 850℃ for 1 h. The superconducting transition temperature ($T_{c,onset}$) of the samples is between 37 K and 38 K. The $T_{c,onset}$ of the sample heat-treated at 600℃ for 40 h is 37 K, whereas the $T_{c,onset}$ of the samples heat-treated at 650℃-850℃ for 1 h is 37.5 K, which is slightly higher than that of the 600℃ sample. The higher $T_{c,onset}$ is attributed to the enhanced formation of a superconducting phase (MgB_2) at high temperatures. No superconducting signal was detected however for the samples heat-treated at above 850℃ because the major formed phase of the samples is MgB_4.

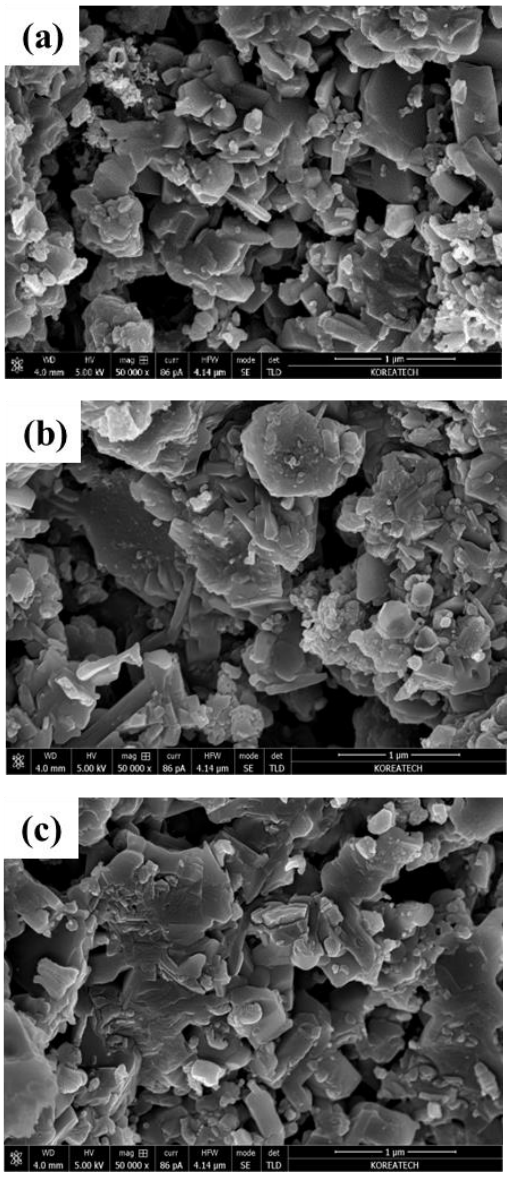

Fig. 5. SEM micrographs of the samples heat-treated at (a) 650℃ for 1 h, (b) 750℃ for 1 h and (c) 850℃ for 1 h.

Fig. 7 shows the J_c-B curve at 5 K and 20 K of the samples heat-treated at 650℃-850℃. The J_c at 5 K of the sample heat-treated at 600℃ for 40 h is the highest. The value of J_c at 5 K and 2 T is 19,600 A/cm^2. The value of J_cs at 5 K and the applied magnetic fields decrease as the heat treatment temperature increases. This is because the grain boundary area, which can be the flux pinning center of MgB_2 [24], is reduced owing to the significant grain growth of MgB_2 at high temperatures, as was previously shown in Figs. 4 and 5.

Unlike the J_c–B characteristics at 5 K, the value of J_c at 20 K below a magnetic field of 3 T of the sample heat-treated at 850℃ is the highest. At a magnetic field of larger than 3 T, there exists a crossover of J_c at 3 T. As a result of the J_c cross over, the value of J_c at 20 K of the sample heat-treated at 650℃ for 40 h is the highest. Further study is needed for understanding the temperature dependence of J_c of MgB_2.

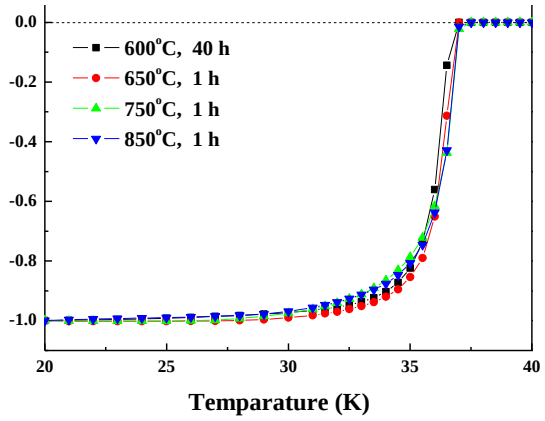

Fig. 6. Normalized susceptibility-temperature curves of samples heat-treat at 650℃-850℃.

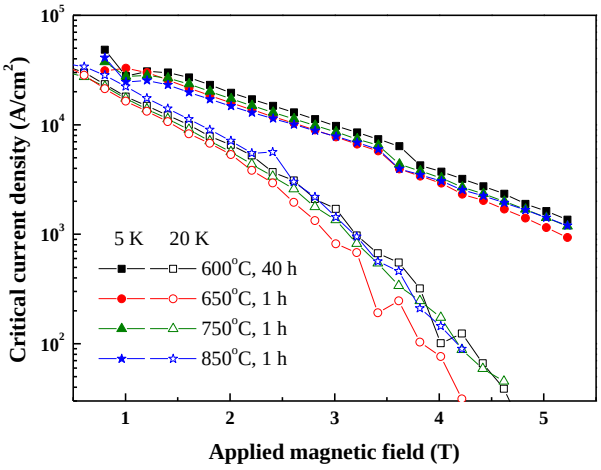

Fig. 7. J_c–B curves of the samples heat-treated at 600℃-850℃.

4. CONCLUSIONS

MgB_2 bulk superconductors were fabricated using a powder reaction process with self-synthesized MgB_4 and commercial Mg powders. At the heat treatment temperature (600℃), which is lower than m. p. of Mg, a prolong heat treat treatment was needed for the formation of MgB_2, whereas at heat treatment temperatures (650℃ -850℃) above m. p. of Mg the formation reaction was completed within 1 h. The enhanced formation of MgB_2 at high temperatures is likely to be due to the fast mass transfer through an Mg melt. The $T_{c,onset}$ of the samples was as high as 37-38 K regardless of the heat treatment temperature. The value of J_c of MgB_2 was dependent on the heat treatment temperature. The value of J_c at 5 K of the sample heat-treated at 600℃ for 40 h was the highest, which is attributed to the smaller grain size of MgB_2. However, the sample heat-treated at 850℃ for 1 h showed the highest J_c at 20 K, and magnetic fields smaller than 3 T. At magnetic fields larger than 3 T, the sample heat-treated at 600℃ for 40 h showed the highest J_c.

ACKNOWLEDGMENT

This work was supported by the National Research Foundation Grant (NRF-2013M2A8A1035822) from Ministry of Science, ICT and Future Planning (MSIP) of Republic of Korea, and partially supported by Korea Institute for Advancement of Technology (KIAT) through the Promoting Regional specialized Industry.

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