Effects of heat treatment temperature on the formation of MgB$_2$ bulk superconductors prepared using MgB$_4$ and Mg powder

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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.

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 conventional 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 μm, spherical in shape) and B (95-97%, average size 1μm) 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°C for 5 h: (a) before and (b) after HNO₃ leaching.

Fig. 2. SEM micrographs of the heat-treated pellets at 1000°C for 5 h: (a) before and (b) after HNO₃ leaching.

The Ti-encapsulated pellets were located at the center of a tubular furnace and heat-treated at 1000°C 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 MgB₄ and undesirable second phases such as MgO and MgB₂, which formed the oxidation of Mg and the low-temperature formation reaction of MgB₂ during heating, were also present (see Fig. 1(a)). To remove the undesirable phases, the crushed powders were put in a 1 mole HNO₃ solution and stirred magnetically for 1 h. The detailed procedure of the HNO₃ leaching process was well described in the literature [19]. It was confirmed in our experiment that most of the MgO and MgB₂ was dissolved completely in the HNO₃ solution, and a high purity MgB₄ powder was obtained (Fig. 1(b)).

Fig. 2 shows scanning electron micrographs (SEM) of the synthesized powders: (a) before and (b) after HNO₃ leaching. Many granular particles, which are considered MgB₂, MgB₄, or MgO particles, are present in sample (a). The size of the formed particles is smaller than 1 μm. After the HNO₃ leaching process, a network structure formed on the surface of the particle agglomerates owing to the dissolution of MgO and MgB₂ in the HNO₃ solution (see sample (b)).

MgB₂ bulk superconductors were made using the synthesized MgB₂ 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 and pestle. 0.3 g of the powder mixture of (Mg+MgB₄) was put in a steel mold with a diameter of 10 mm and uniaxially pressed into a pellet. Some pellets were heat-treated at 600°C for a prolonged period of 40 h, and others were heat-treated at 650°C-1050°C for a short period of 1 h in flowing argon gas. Because a melting temperature of Mg is 650°C, the formation reaction of MgB₂ below 650°C will be slowly achieved through a solid state reaction by eq. (1-1), whereas the formation reaction above 650°C will rapidly be achieved through the liquid state reaction according to eq. (1-2).

Below 650°C: MgB₄ + Mg (solid) = 2MgB₂  (1-1)

Above 650°C: MgB₄ + Mg (liquid) = 2MgB₂  (1-2)

To measure $T_c$ and $J_c$ of MgB₂ bulk samples, rectangular specimens with an approximate dimension of 3x3x2 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)

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

where $\Delta M$ 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°C-1050°C. The major formed phase of samples prepared at 600°C for 40 h and at 650°C-850°C for 1 h are MgB₂, whereas a major formed phase above 860°C is MgB₄. This is because MgB₂ is a stable phase at a high temperature. In addition to the presence of MgB₄, 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 MgB₂ of the prepared samples is qualitatively analyzed from the peak intensity of MgB₂ in the XRD patterns. The peak intensity level of MgB₂ of the samples heat-treated at 650°C-850°C for 1 h is almost the same as that of the sample heat-treated at 600°C for 40 h. This indicates that the formation reaction of MgB₂ 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 MgB₂ among the samples prepared at 600°C-850°C, 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 MgB₂.

The grain size (crystallite size) of MgB₂ was calculated from eq. (3) [23] using the data of FWHM of XRD peaks.

\[ t = 0.9\lambda/B\cos\theta \]  

(3)

where \( t \) is the grain size, \( \lambda \) is the wavelength of the target used, \( B \) is the half width of a peak and \( \theta \) is the angle of an incident beam.

Fig. 4 shows grain size of MgB₂ as a function of heat treatment temperature. As can be seen in the figure, the grain size of MgB₂ increases as the heat treatment temperature increases. The grain size of MgB₂ heat-treated at 600°C for 40 h is 70 nm, whereas the grain sizes of MgB₂ heat-treated at 650°C, 750°C, 850°C and 950°C 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 MgB₂, as well as the accelerated formation reaction of MgB₂ [13].

Fig. 4. Grain size of MgB₂ as a function of heat treatment temperature.

Table 1. Lattice parameters \( a \) and \( c \), and full width half maximum of MgB₂ heat-treated at various temperatures.

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

Fig. 5 shows SEM micrographs of the samples heat-treated at (a) 650°C for 1 h, (b) 750°C for 1 h, and (c) 850°C 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 MgB₂. It is, therefore, reasonable that 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°C for 40 h, 650°C for 1 h, 750°C for 1 h and 850°C 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°C for 40 h is 37 K, whereas the \( T_{c, onset} \) of the samples heat-treated at 650°C-850°C for 1 h is 37.5 K, which is slightly higher than that of the 600°C sample. The higher \( T_{c, onset} \) is attributed to the enhanced formation of a superconducting phase (MgB₂) at high temperatures. No superconducting signal was detected however for the samples heat-treated at above 850°C because the major formed phase of the samples is MgB₄.

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Lattice parameters \( a \) and \( c \), and full width half maximum of MgB₂ heat-treated at various temperatures.

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Fig. 5. Powder X-ray diffraction patterns of the samples prepared under various heat treatment conditions.
Fig. 5. SEM micrographs of the samples heat-treated at (a) 650°C for 1 h, (b) 750°C for 1 h and (c) 850°C for 1 h.

Fig. 7 shows the $J_c$-B curve at 5 K and 20 K of the samples heat-treated at 650°C-850°C. The $J_c$ at 5 K of the sample heat-treated at 600°C for 40 h is the highest. The value of $J_c$ 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°C 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°C for 40 h is the highest. Further study is needed for understanding the temperature dependence of $J_c$ of MgB$_2$.

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°C), which is lower than m. p. of Mg, a prolong heat treatment was needed for the formation of MgB$_2$, whereas at heat treatment temperatures (650°C-850°C) 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°C for 40 h was the highest, which is attributed to the smaller grain size of MgB$_2$. However, the sample heat-treated at 850°C 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°C for 40 h showed the highest $J_c$. 
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REFERENCES

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani and J. Akimitsu, “Superconductivity at 39 K in magnesium diboride,” Nature, vol. 410, pp. 63-64, 2001.
[2] Y. Eltsev, S. Lee, K. Nakao, N. Chikumoto, S. Tajima, N. Koshizuka and M. Murakami, “Anisotropic superconducting properties of MgB$_2$ single crystals probed by in-plane electrical transport measurements,” Phys. Rev., vol. 65, pp. 140501, 2002.
[3] Zongping Ma, Yongchang Liu, Lining Yu and Qian Zhao, “The accelerated formation of MgB$_2$ phase with high critical current density by Cu and SiC multidoping during the low-temperature sintering process,” J. Appl. Phys., vol. 104, pp. 113917, 2008.
[4] V. Grinenko, E. P. Krasnopetrova, V. A. Stoiarova, A. A. Bush and B. P. Mikhailov, “Superconductivity in porous MgB$_2$,” Physics C, vol. 43, pp. 492–495, 2006.
[5] A. V. Pan, S. Zhou, H. Liu and S. Dou, “Properties of superconducting MgB$_2$ wires: in situ versus ex situ reaction technique,” Supercond. Sci. Technol., vol. 16, pp. 639-644, 2003.
[6] C. U. Jung, M. S. Park, M. S. Kim, J. H. Choi, W. N. Kang, H. P. Kim and S. I. Lee, “High-pressure sintering of highly dense MgB$_2$ and its unique pinning properties,”Curr. Appl. Phys., vol. 1, pp. 327-331, 2001.
[7] B. A. Glowacki, M. Majoros, M. Vickers, J. E. Evetts, Y. Shi and I. Mcdougall, “Superconductivity of powder-in-tube MgB$_2$ wires,” Supercond. Sci. Technol., vol. 14, pp. 193-199, 2001.
[8] A. Tampieri, G. Celotti, S. Spinro, R. Caciuflfo and D. Rinaldi, “Study of the sintering behavior of MgB$_2$ superconductor during hot-pressing,” Physica C, vol. 400, pp. 97-104, 2004.
[9] E. Martinez, L. A. Angurel and R. Navarro, “Study of Ag and Cu/MgB$_2$ powder-in-tube composite wires fabricated by In situ reaction at low temperature,” Supercond. Sci. Technol., vol. 15, pp. 1043-1047, 2002.
[10] B. H. Jun and C. J. Kim, “The effect of heat-treatment temperature on the superconducting properties of malic acid-doped MgB$_2$/Fe wire,” Supercond. Sci. Technol., vol. 20, pp. 980-985, 2007.
[11] J. H. Kim, S. X. Dou, J. L. Wang, D. Q. Shi, X. Xu, M. S. A. Hossain, W. K. Yeoh, S. Choi and T. Kiyoshi, “The effects of sintering temperature on superconductivity in MgB$_2$/Fe wires,” Supercond. Sci. Technol., vol. 20, pp. 448-451, 2007.
[12] A. Yamamoto, J. I. Shimoyama, Y. Ueda, Y. Katsura, S. Horii and K. Kishio, “Improved critical current properties observed in MgB$_2$ bulk synthesized by low-temperature solid-state reaction,” Supercond. Sci. Technol., vol. 18, pp. 116-121, 2004.
[13] B.-H. Jun, N.-K. Kim, K.S. Tan and C.-J. Kim, “Enhanced critical current properties of in situ processed MgB$_2$ wires using milled boron powder and low temperature solid-state reaction,” J. Alloys Compd., vol. 492, pp. 446-451, 2010.
[14] A. Serquis, Y. T. Zhu, E. J. Peterson, J. Y. Coulter, D. E. Peterson, and F. M. Mueller, “Effect of lattice strain and defects on the superconductivity of MgB$_2$,” Amer. Inst. phys. vol. 79, pp. 4399-4401, 2001.
[15] C. J. Kim, J. H. Yi, B. H. Jun, B. Y. You, S. D. Park and K. N. Choo, “Reaction-induced pore formation and superconductivity in in situ processed MgB$_2$ superconductors,” Physica C., vol. 502, pp. 4–9, 2014.
[16] K. L. Tan, K. P. Lim, A. S. Halim and S. K. Chen, “Enhanced critical current density in MgB$_2$ prepared by reaction of MgB$_2$ and Mg,” Phys. Status Solidi A., vol. 210, No. 3, pp. 616–622, 2013.
[17] D Nardelli, D Materia, M Vignolo, G Bovone, A. Palenzona, A. S. Siri and G. Grasso, “Large critical current density in MgB$_2$ wire using MgB$_2$ as precursor,” Supercond. Sci. Technol., vol. 26, pp. 075010, 2013.
[18] A. Ito, A. Yamamoto, J. Shimoyama, H. Ogino and K. Kishio, “Synthesis of dense in situ MgB$_2$ bulks using MgB$_2$ precursor,” IEEE Trans. Appl. Supercond., vol. 23, pp. 7101005, 2013.
[19] K. L. Tan, K. Y. Tan, K. P. Lim, S. A. Halim and S. K. Chen, “Synthesis of MgB$_2$ from MgB$_2$ through combinatorial solid state reaction routes,” Solid state. Sci. Tech., vol. 19, pp. 15–19, 2011.
[20] J. Ishiwata, M. Muralidhar, K. Inoue and M. Murakami, “Effect of MgB$_2$ addition on the superconducting properties of polycrystalline MgB$_2$,” Physica Procedia., vol. 65, pp. 69–72, 2015.
[21] K. S. Tan, B. H. Jun and C. J. Kim, “Superconducting properties of a MgB$_2$ bulk formed by using a MgB$_2$ + Mg Mixture,” J. Korean Phys. Soc., vol. 54, No. 4, pp. 1626-1629, 2009.
[22] C. P. Bean, “Magnetization of high-field superconductors,” Rev. Mod. Phys., vol. 36, pp. 31-39, 1964.
[23] P. Scherrer, “Bestimmung der grösse und der inneren struktur von kolloidteilchen mittels röntgenstrahlen,” Nachr. Ges. Wiss. Göttingen, vol. 26, pp. 98-100, 1918.
[24] J. H. Yi, K. T. Kim, B. H. Jun, J. M. Sohn, B. G. Kim, J. Joo and C. J. Kim, “Pore formation in in situ processed MgB$_2$ superconductors,” Physica C, vol. 469, pp. 1192–1195, 2009.