A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 60 2015 Issue 2
DOI: 10.1515/amm-2015-0112

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PROPERTIES OF MgB_2/Ga COMPOSITES PREPARED BY MECHANICAL ALLOYING

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In this study, we examined the effect of Ga-doping and mechanical alloying in MgB_2 on microstructural and phase evolution. A comparison was made between *in-situ* and *ex-situ* processed Mg-B-Ga samples. Densification was markedly improved by *ex-situ* sintering of ball-milled MgB_2+Ga. The Ga-doping and ball-milling prior to sintering resulted in the formation of impurity phases such as MgO, Ga_5Mg_2 and Ga_2O_3. Lattice parameter of MgB_2 increased with increasing ball-milling duration as well as by Ga-doping.

Keywords: Magnesium diboride, superconductors, mechanical alloying, ball-milling

1. Introduction

MgB_2 has many advantageous features over conventional oxide-based or metallic superconductors [1,2,3]. Compared to A-15 superconducting compounds such as Nb_3Sn or NbTi, for instance, its transition temperature (T_c =39K) is high enough to be operated with cryogenic coolers avoiding the use of expensive liquid helium. Furthermore, the synthesis of MgB_2 is relatively easy with compositional tolerance. Grain boundary weak-link associated with anisotropy which intrinsically hinders transport properties in oxide-based superconductors, is not a serious issue in MgB_2. Other advantages include low cost of raw materials and light weight. MgB_2 is thus considered as an important material for many superconducting devices such as a magnetic resonance imaging (MRI) system.

However, two major problems should be overcome or at least minimized for the practical application and wide use of MgB_2. First, sintered MgB_2 usually shows a poor densification with a large amount of intergranular pores which results in low critical current density [4,5]. So far, two methods have been commonly employed for the synthesis of MgB_2: *in-situ* reaction of elemental Mg and B powders, and *ex-situ* method using pre-alloyed compound as a starting material. The former is fast and suitable for doping, but has difficulties in controlling highly volatile and reactive Mg during sintering. The latter method has advantage to control purity and grain sized, but results in a poor densification. The second issue of MgB_2 is insufficient flux pinning property, in particular at high magnetic fields. It has been known that this problem can be largely improved by two approaches: doping or mechanical alloying [6,7]. The distortion of lattice by chemical doping or the introduction of lattice defects by ball-milling are known to effectively pin flux lines, enhancing superconducting properties of MgB_2.

In the present work, we attempted simultaneously both doping and mechanical alloying to optimize microstructures and phase formation of MgB_2 for the possible enhancement of superconducting property. For the doping and alloying of MgB_2, Ga was chosen due to its low melting point (29.8°C). Both *in-situ* and *ex-situ* sintering were attempted as well.

2. Experimental

The starting materials were Mg powder (>99%, -40 mesh) from Riedel-de Haen Co., crystalline B powder (>99%, 2μm) from Merck Co., MgB_2 powder (99%, -100 mech) from Aldrich Co. and Ga granules (4N, 2 mm) from Strem Chemicals Co. Ga-doped MgB_2 was prepared by two different ways. First, the elemental material mixture of B+Ga (atomic ratio of 1.9:0.1) was ball-milled. And then the ball-milled B+Ga powders were mixed with Mg powder to give a composition of $MgB_{1.9}Ga_{0.1}$, followed by subsequent sintering (*in-situ* method). Second, the prealloyed MgB_2 was mixed with Ga to the composition of $MgB_2Ga_{0.1}$, and then ball-milled, followed by sintering (*ex-situ* method). The examined materials and compositions are summarized in Table 1. The ball-milling was carried out for 12, 24 and 48 h using a horizontal mill at 40°C. At this temperature, Ga whose m.p. is 29.8°C was in liquid state. The milling vial and balls were hardness stainless steel. The ball-to-powder weight ratio was 200 :1. The rotating speed of milling vial was 30 r.p.m. The processed powders were die-compacted using hydraulic press and put in a tubular furnace for 3 h in an argon atmosphere at 700°C. The samples were examined by X-Ray Diffractometer (XRD, Ulitma IV) using CuK_α radiation. The phase identification and lattice parameters were analyzed by Rietvelt refinment method.

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The microstructure was examined by Scanning Electron Microscopy (SEM, VEGA II LMU).

TABLE 1
Compositions and preparation conditions of examined samples

Sample	Compositions	Milling time	Remarks
No.1	$MgB_{1.9}Ga_{0.1}$	12h	In-situ sintering of Mg and ball-milled B+Ga + Mg
No.2	$MgB_{1.9}Ga_{0.1}$	24h	”
No.3	$MgB_{1.9}Ga_{0.1}$	48h	”
No.4	$MgB_2Ga_{0.1}$	12h	Ex-situ sintering of ball-milled MgB_2+ Ga
No.5	$MgB_2Ga_{0.1}$	24h	”
No.6	$MgB_2Ga_{0.1}$	48h	”

3. Results and discussion

Fig. 1 shows the XRD patterns of *in-situ* processed (sintered) $MgB_{1.9}Ga_{0.1}$.(samples No.1~3) Time indicated in the graph represents the ball-milling duration of B+Ga mixture, prior to sintering. In all samples, superconducting MgB_2 phase formed after sintering of Mg and ball-milled B+Ga. However,

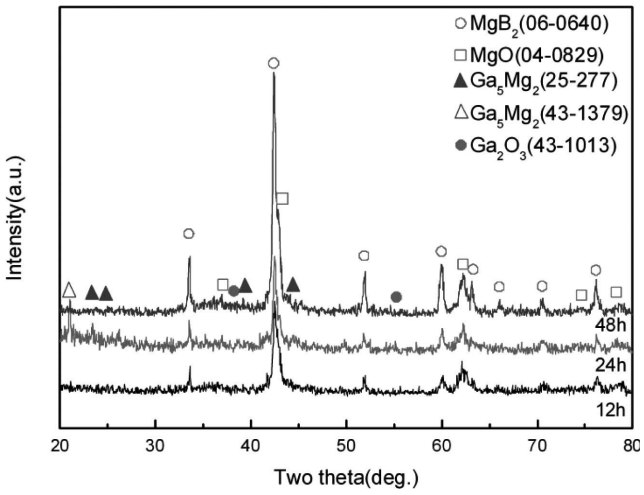

Fig. 1. XRD patterns of in-situ processed $MgB_{1.9}Ga_{0.1}$. (No.1~3) (Time: ball-milling duration)

the increase in milling duration promotes the formation of non-superconducting impurity phases such as MgO, Ga_5Mg_2 and Ga_2O_3. The formation of the impurity phases was more apparently visible for the sample ball-milled for 24 h than that milled for 48 h. This might attribute to the broadening and weakening of crystalline peaks, induced by intensive ball-milling. On the other hand, for sample No.1 which was moderately milled for 12 h, the superconducting MgB_2 is a major phase with a small amount of MgO which is known to form almost inevitably during *in-situ* reaction (sintering) in Mg-B system. A similar tendency was also observed in *ex-situ* processed $MgB_2Ga_{0.1}$.(samples No.4~6) In these samples as well, the amount of Ga_5Mg_2 and Ga_2O_3 increased with increasing the milling duration of MgB_2+Ga mixture. In particular, the amount of MgO phase increased considerably during milling.

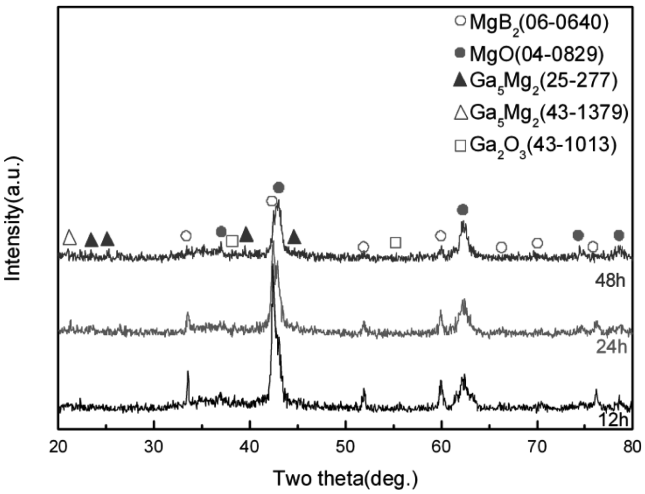

Fig. 2. XRD patterns of ex-situ processed $MgB_2Ga_{0.1}$. (No.4~6) (Time: ball-milling duration)

This can be clearly seen in Fig. 3 where the relative XRD peak intensity of MgO(200)/MgB_2(101) is represented. The amount of MgO phase considerably increased with increasing ball-milling duration for *ex-situ* processed samples. MgO was even the major phase for the sample milled for 48 h. On the other hand, for *in-situ* processed samples the MgO phase slightly decreased rather than increased with ball-milling duration.

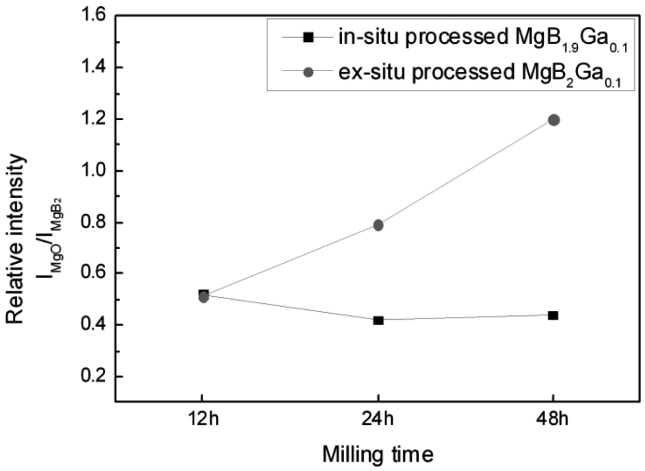

Fig. 3. Relative XRD peak intensity of MgO(200)/MgB_2(101)

To clarify this, we examined the fracture surface of both *in-situ* and *ex-situ* processed samples. For comparison, a typical SEM morphology of pristine MgB_2 (without Ga doping and prior to ball-milling), which was prepared under same sintering condition as samples No.1~6, was represented in Fig. 4. As shown in the micrograph, many large pores of several tens microns are visible (Fig. 4a). These pores were formed by gas (mainly oxygen) which was released during melting of Mg and trapped during solidification. The observed microstructure is quite typical in *in-situ* sintering of elemental Mg-B mixture at temperature above the m.p. of Mg. Besides the large pores, a higher magnification image (Fig. 4b) shows that non-pore regions are composed of very fine crystalline grains of MgB_2

with a considerable amount of interstices between them. It is well-known that the existence of large pores together with tiny interstices between grains hinder superconducting transport property.

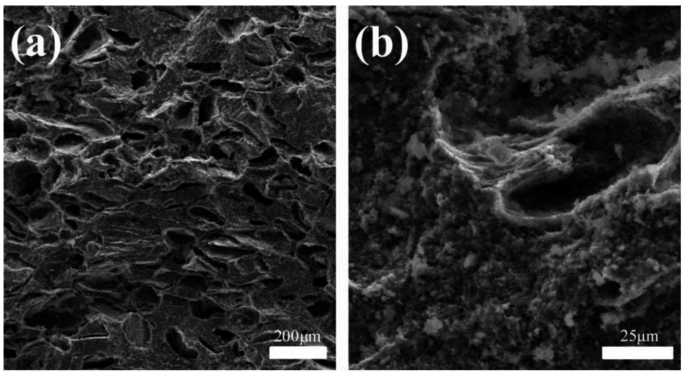

Fig. 4. Fractured surface images of sintered MgB_2. (b: higher magnification image)

In Fig. 5, the fractured surface of *in-situ* processed samples No.1~3 (a~c) and *ex-situ* processed samples No.4~6 (d~f) are compared. As shown in the micrographs, large pores persist in *in-situ* processed samples No.1~3 (a~c). On the other hand, they completely disappeared for *ex-situ* processed samples No.4~6 (d~f). This can be seen also at a higher magnification images (Fig. 6). The result of sintered density measurement clearly confirms the observed microstructures. The combined processing of ball-milling and Ga-doping, followed *ex-situ* sintering, resulted in a highly dense MgB_2 materials. The sintered density of samples No.4~6 was 30~40% higher than that of samples No.1~3. The observed high densification in Ga-doped and ball-milled samples can be hardly achieved by conventional *ex-situ* sintering of MgB_2.

The lattice parameter of MgB_2 phase was analyzed for samples No.1~6. In general, the value increased with increasing milling duration. The *ex-situ* sample exhibited a higher increase than the *in-situ* samples. It is known that the lattice expansion or distortion generally enhance flux pinning effect, improving superconducting properties.

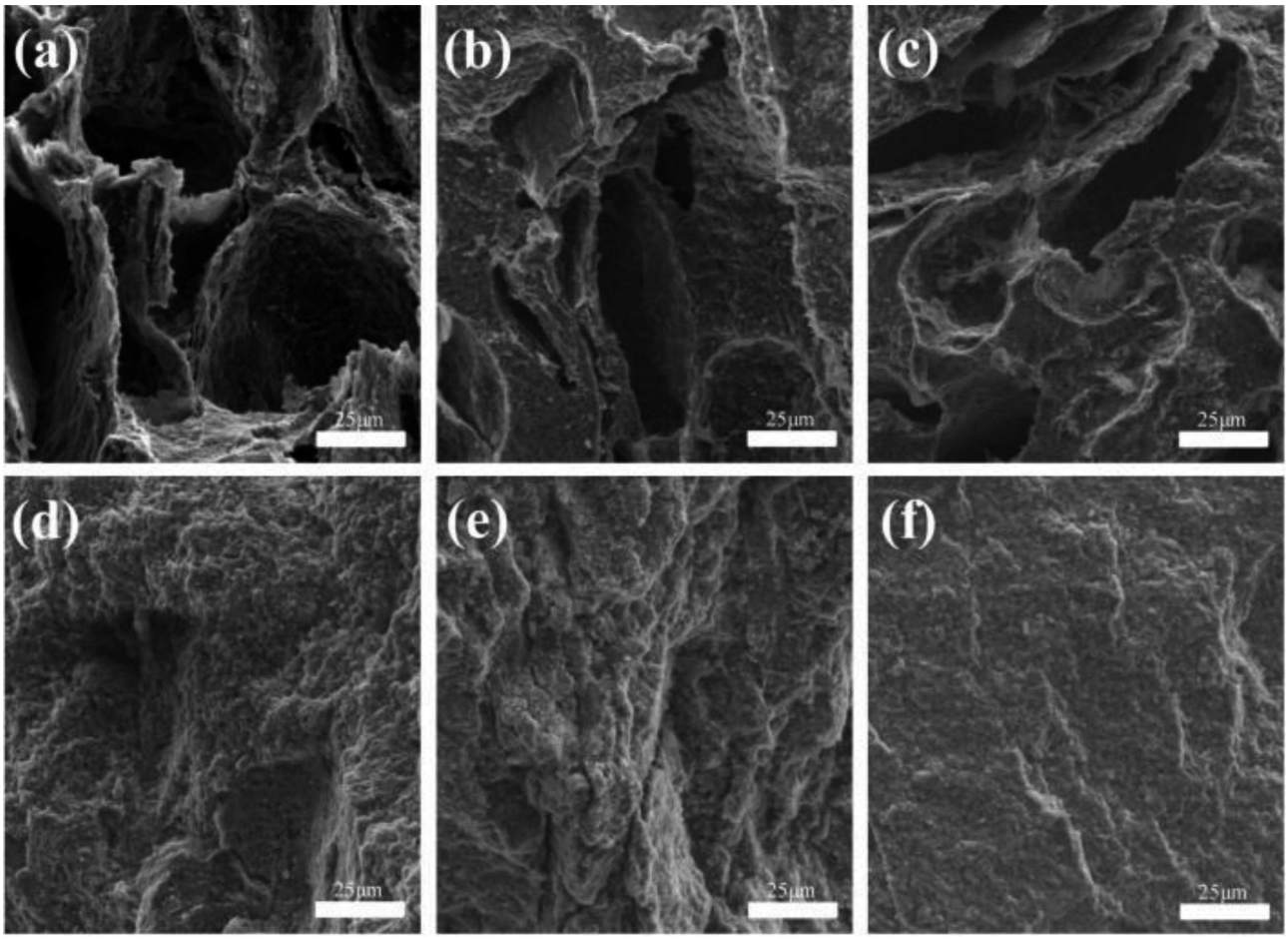

Fig. 5. Effect of ball-milling time on fractured micrographs. (a)~(c): in-situ processed samples No.1~3. (d)~(f): ex-situ processed samples No.4~6

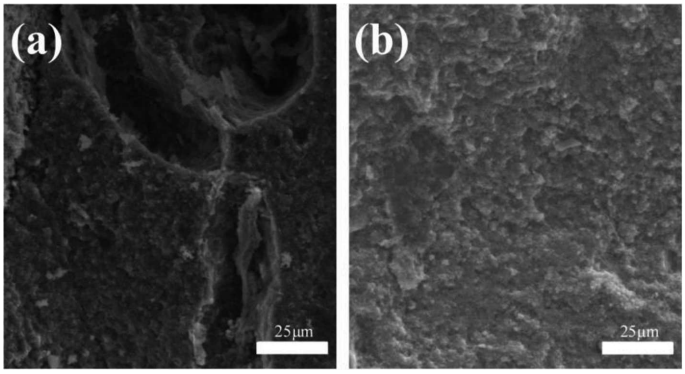

Fig. 6. Fractured micrographs at higher magnification: (a) in-situ processed sample No.2 and (b) ex-situ processed sample No. 6

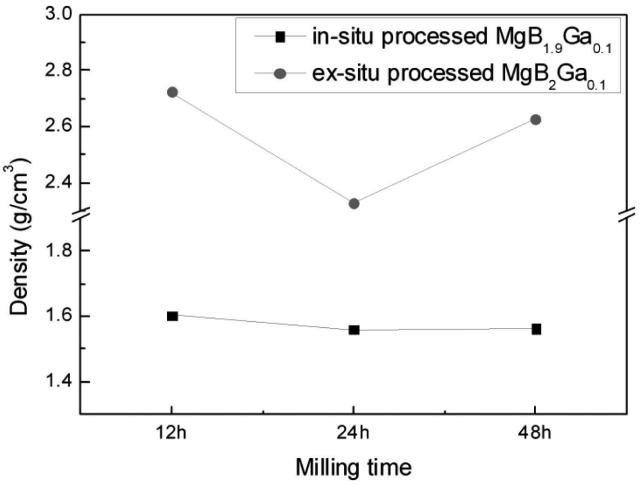

Fig. 7. Effect of milling time on the sintered density of samples. (No.1~6)

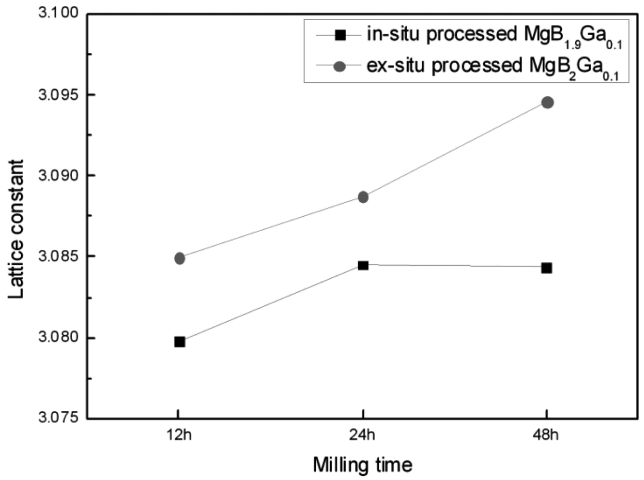

Fig. 8. Effect of milling time on the lattice parameter a of MgB_2 phase

4. Conclusions

In this study, we examined the combined effect of Ga-doping and ball-milling to optimized the microstructures and phase formation of MgB_2 for eventual enhancement of superconducting properties. Densification was markedly improved by *ex-situ* sintering of ball-milled MgB_2+Ga. The Ga-doping and ball-milling prior to sintering resulted in the formation of impurity phases such as MgO, Ga_5Mg_2 and Ga_2O_3. Although non-superconducting phases Ga_5Mg_2 and Ga_2O_3 are thought to be detrimental for critical current density, the existence of a certain amount of MgO might enhance flux pinning property of MgB_2. The detailed superconducting properties in terms of impurity phases in the present work are under examination.

Acknowledgements

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2013R1A1A2A10008205).

REFERENCES

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, Nature. **410**, 63 (2001).
[2] D.G. Lee, J.H. Lee, B.H. Jun, S.D. Park, Y.R. Uhm, H.W. Park, C.J. Kim, J. Kor. Powd. Met. Inst. **19**, 2 (2012).
[3] D.K. Kang, S.H. Choi, I.S. Ahn, J. Kor. Powd. Met. Inst. **15**, 5 (2008).
[4] X. Xu, J.H. Kim, W.K. Yeoh, Y. Zhang, S.X. Dou, Supercond. Sci. Technol. **19**, 47 (2006).
[5] K. Shinohara, T. Futatsumori, H. Ikeda, Physica C. **468**, 1369 (2008).
[6] Y. Zhang, S.H. Zhou, X.L. Wang, S.X. Dou, Physica C. **468**, 1383 (2008).
[7] G. Serrano, A. Serquis, D. Rodrigues Jr., M.T. Malachevsky, J.M. Espasandin, C. Ayala, J. Phys. Conf. Ser. **97**, 0121271 (2008).

Received: 20 November 2014.