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$_2$Mg$_4$, and Ga$_2$O$_3$. 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$_3$Sn 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$_2$Ga$_{0.1}$, 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-compact 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, Ultima IV) using CuK$_{α}$ radiation. The phase identification and lattice parameters were analyzed by Rietveld refinement method.
The microstructure was examined by Scanning Electron Microscopy (SEM, VEGA II LMU).

### TABLE 1

| Sample | Compositions | Milling time | Remarks |
|--------|--------------|--------------|---------|
| No.1   | MgB₁₉Ga₀₁₀₁ | 12h          | In-situ sintering of Mg and ball-milled B+Ga + Mg |
| No.2   | MgB₁₉Ga₀₁₀₁ | 24h          | "         |
| No.3   | MgB₁₉Ga₀₁₀₁ | 48h          | "         |
| No.4   | MgB₂Ga₀₁₀₁  | 12h          | Ex-situ sintering of ball-milled MgB₂+Ga |
| No.5   | MgB₂Ga₀₁₀₁  | 24h          | "         |
| No.6   | MgB₂Ga₀₁₀₁  | 48h          | "         |

3. Results and discussion

Fig. 1 shows the XRD patterns of in-situ processed (sintered) MgB₁₉Ga₀₁₀₁. (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 MgB₂ phase formed after sintering of Mg and ball-milled B+Ga. However, the increase in milling duration promotes the formation of non-superconducting impurity phases such as MgO, Ga₅Mg₂ and Ga₂O₃. 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 MgB₂ 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 MgB₂Ga₀₁₀₁. (samples No.4~6) In these samples as well, the amount of Ga₅Mg₂ and Ga₂O₃ increased with increasing the milling duration of MgB₂+Ga mixture. In particular, the amount of MgO phase increased considerably during milling.

![Fig. 1. XRD patterns of in-situ processed MgB₁₉Ga₀₁₀₁. (No.1~3) (Time: ball-milling duration)](image)

This can be clearly seen in Fig. 3 where the relative XRD peak intensity of MgO(200)/MgB₂(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. 2. XRD patterns of ex-situ processed MgB₂Ga₀₁₀₁. (No.4~6) (Time: ball-milling duration)](image)

![Fig. 3. Relative XRD peak intensity of MgO(200)/MgB₂(101)](image)

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 MgB₂ (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 MgB₂.
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.

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. 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$_5$Mg$_2$ and Ga$_2$O$_3$. Although non-superconducting phases Ga$_5$Mg$_2$ and Ga$_2$O$_3$ 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.

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