Dramatic effects of Ag addition on low temperature synthesis of MgB$_2$

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Abstract. We have recently discovered that small amount Ag addition is effective in lowering formation temperature of MgB$_2$ from a powder mixture Mg and B. In the present paper, synthesis and superconducting properties of Ag-added and Ag- and SiC-added MgB$_2$ bulks, Ag-added MgB$_2$ tapes and a dense Ag-added MgB$_2$ bulk are summarized. C-substitution for the MgB$_2$ phase was confirmed to occur even for a sample reacted at 550°C by Ag-addition. For “in-situ” Fe-sheathed MgB$_2$ tapes, reaction temperature to obtain strongly grain coupled MgB$_2$ core was decreased down to 500°C by Ag-addition. Moreover, a dense MgB$_2$ bulk was synthesized by the PICT-diffusion method performed at 700°C for 72 h. In all these studies, Ag-addition was found to be effective to decrease the processing temperatures without serious degradation of $T_c$ and critical current properties. Our results suggest that small amount of Ag-addition is a promising way to develop low cost and high performance MgB$_2$ materials.

1. Introduction
Numerous researches and developments have been made for practical applications of MgB$_2$ as tapes and wires since the discovery its superconductivity [1]. The main application targets for long MgB$_2$ conductors are supposed to be superconducting magnets installed in MRI systems and MAGLEV trains operating at 15-20 K. Although long MgB$_2$ conductors have been developed at several companies, further improvement of $J_c$ characteristics is still needed for their extensive practical applications.

There are two major methods adopted to fabricate metal-sheathed MgB$_2$ wires and tapes, which are “in-situ” and “ex-situ” methods. In the “in-situ” method, cold-worked wires or tapes containing a powder mixture of Mg and B are heated for phase formation of MgB$_2$. On the other hand, the already-made MgB$_2$ powder is used in the “ex-situ” method. Critical current properties are usually higher for the “in-situ” processed tapes because of strong grain coupling in the resulting MgB$_2$ core.

The reaction forming MgB$_2$ phase from a powder mixture of Mg and B occurs by diffusion of Mg into B powder without increasing bulk density unless high pressures are applied. Since grain size of Mg (typically several tens µm) is much larger than that of B (less than 1 µm), many long voids parallel
to the drawing direction remain at places where starting Mg occupied in the “in-situ” processed tapes, resulting in low bulk density approximately half of the theoretical value. Therefore, improvement of density is one of the important subjects to enhance \( J_c \). In fact, highly dense MgB\(_2\) bulks prepared by the PICT-diffusion method [2] showed high \( J_c \) exceeding 1 MA cm\(^{-2}\) at 20 K in low fields [3].

On the other hand, the grain boundary in MgB\(_2\) is recognized as predominant pinning site through the studies done for polycrystalline thin films [4], tapes [5] and bulks [6,7]. A strong proportional relationship between the maximum flux pinning force density, \( F_{p(max)} \), and inverse grain size was confirmed for polycrystalline MgB\(_2\) in our previous study [7]. A similar tendency was also confirmed for carbon-substituted MgB\(_2\) bulks [8]. In addition, in-plane crystallinity plays a crucial role in determining the pinning strength at grain boundaries through changes in the coherence length [9]. In addition, substitution of C for the B-site is effective for improving in-field \( J_c \) mainly by lowering in-plane crystallinity.

Above facts on the determining \( J_c \) characteristics of polycrystalline MgB\(_2\) suggest that reaction at low temperatures using fine B powder, C-doping and densification are effective approaches for development of MgB\(_2\) polycrystalline conductors with enough high critical current properties for practical use. The low temperature synthesis of MgB\(_2\) is also preferable for reduction of fabrication cost.

Reaction of the “in-situ” MgB\(_2\) conductors has been done at a temperature of 600–900°C, because reaction between Mg and B are quite sluggish below 600°C. In our previous study, reaction of Mg and B at 550°C required a very long time (600 h) for the complete reaction to form the MgB\(_2\) phase [10]. Although the mechanical alloying promotes formation of the MgB\(_2\) phase without intentional heating, the additional heating process above 600°C was indispensable to perform complete reaction between Mg and B for forming MgB\(_2\) [11]. In the case of the “in-situ” processed tapes, reaction temperature between Mg and B is generally lowered compared with that of the bulks because of the dense contact part of Mg and B after drawing tapes, i.e. the short diffusion length of Mg to form MgB\(_2\) phase. Removal of thin MgO layer covering Mg grains by drawing also contributes for formation of MgB\(_2\) in a short time. In fact, a MgB\(_2\) tape was successfully synthesized by heating at ~500°C using the mechanically alloyed powder [12]. However, unintentional contaminations from milling balls cannot be prevented in this method. Using Mg hydride [13] or fine Mg [14,15] as starting powder is also known to be effective for lowering synthesis temperature of the MgB\(_2\) tapes. However, heating above 600°C is again needed to achieve strong grain coupling leading to their high \( J_c \) characteristics.

In our previous study, small amount of Ag addition was found to be effective for a decrease of reaction temperature between Mg and B down to approximately 500°C [16]. Added Ag lowers melting point of Mg, resulting in enhancement of Mg reactivity to form MgB\(_2\). This technique can be easily extended for the synthesis of MgB\(_2\) tapes for practical use.

Based on these backgrounds, Ag-doped MgB\(_2\) tapes were synthesized by the low temperature reaction in the present study. In addition, Ag-aded and C-doped MgB\(_2\) bulks and highly dense Ag-added MgB\(_2\) bulks were prepared by low temperature reaction and the PICT-diffusion method, respectively.

2. Experimental

Bulk samples of MgB\(_2\) were prepared by the PICT (powder-in-closed-tube) method using stainless steel (SUS316) as a sheath material [17]. Starting powders were Mg (99.5% purity, 45 µm in size), B (99%, ~300 nm) and Ag (99%, ~ 100 nm). These powders were mixed in a molar ratio of Mg : B : Ag = 1.1 + x : 2 : x with \( x = 0 - 0.15 \). Then each powder mixture was filled in a one-end-closed stainless tube (SUS316), uniaxially pressed into tape shape and the other end sealed by pressing. A SiC-doped MgB\(_2\) bulk with a nominal composition of Mg\(_{1.13}\)B\(_2\)Ag\(_{0.03}\)SiC\(_{0.04}\) was prepared by the same method. The Fe-sheathed MgB\(_2\) tapes with mono core were synthesized by the “in-situ” method. Powder
mixtures of Mg, B and Ag with nominal compositions of Mg : B : Ag = 1 + 3x : 2 : x (x = 0, 0.02) were filled in Fe tubes with inner/outer diameters of 3.2 mm/6.2 mm. By drawing and rolling, raw tapes with ~4 mm in width and ~0.5 mm in thickness were obtained. After sealing these samples into evacuated quartz ampoules, heat-treatment was performed for 24~72 h at various temperatures.

A dense Ag-added MgB$_2$ tape was prepared by the PICT-diffusion method [2]. Diffusion of Mg+0.1Ag into a pressed powder mixture of B and MgB$_2$ (commercial powder: Furuuchi) with a molar ratio of 2 : 1 was attempted at 700°C for 72 h in a closed SUS316 tube, which was sealed a quartz ampoule.

Constituent phases of the resulting samples were analyzed by powder x-ray diffraction (XRD) measurements. Microstructure and superconducting properties of the samples were examined by a scanning electron microscope equipped with an energy dispersive X-ray spectrometer and a SQUID magnetometer, respectively. $J_c$ of each sample was calculated from dimension of the examined bulk and width of the magnetization hysteresis loop based on the extended Bean model.

3. Results and Discussions

3.1 Low temperature synthesis of MgB$_2$ bulks by Ag-addition.

The moderate amount of Ag in the MgB$_2$ bulk was found to be $x = 0.02$–0.05 in the nominal chemical formula of Mg$_{1.1+x}$B$_2$Ag$_x$, in our previous study [16]. From these nominal compositions, completely reacted MgB$_2$ bulks were obtained by heating at 550°C for 72 h. As shown in Fig. 1, a Ag-added sample with $x = 0.03$ was composed of MgB$_2$ as the main phase, while a Ag-free sample contained a large amount of unreacted Mg. After the heat-treatment, a binary alloy, Mg-Ag, was formed at the edge of voids in the bulk. Therefore, Ag-addition did not degrade strongly connected MgB$_2$ networks, resulting in high $J_c$ performance.

SiC is the most popular C source for preparation of C-doped MgB$_2$, because its commercial fine powders are easily obtained and it decomposes below 600°C to form Mg$_2$Si and active C is released at the same time. Therefore, C-doped MgB$_2$ bulks or tapes can be obtained by heating at 600°C using SiC as a carbon source. However, actual substitution level in the MgB$_2$ is usually much lower than the nominal level and it strongly depends on reaction temperature and holding time. Note that the C-substituted MgB$_2$ bulk has never been prepared at lower temperatures than 600°C.

![Figure 1. Powder XRD patterns of Ag-free, Ag-added and SiC-added MgB$_2$ bulks reacted at 550°C for 72 h. The inset shows their 110 peaks.](image1)

![Figure 2. $J_c$-H characteristics of Ag-added and Ag- and SiC-added MgB$_2$ bulks reacted at 550°C for 72 h. Their ZFC curves are shown in the inset.](image2)
As shown in Fig. 1, Ag- and SiC-added MgB₂ bulk was successfully synthesized by heating at 550°C for 72 h. The 110 peaks shifted to higher angle by the SiC-addition as indicated in the inset. The $a$-axis lengths of Ag-added and Ag- and SiC-added MgB₂ bulks were 3.085 and 3.080 nm, respectively. The shorter $a$-axis length of SiC-added sample than that of the SiC-free tape is an evidence of partial substitution of C for B-site in MgB₂. Figure 2 shows $J_c$-$H$ characteristics of Ag-added and Ag- and SiC-added MgB₂ bulks at 20 K. Enhancement of $J_c$ under high fields by SiC-addition is a common feature of C-substituted MgB₂. It should be noted that decrease in $T_c$ by ~1 K and shortening of $a$-axis by 0.005 nm suggested that approximately half of C contained in SiC substituted for B-site of MgB₂ in the resulting sample.

3.2 Fabrication and Characteristics of Ag-added MgB₂ tapes

Figure 3 shows powder XRD patterns of the Ag-free and Ag-added MgB₂ tapes. Even including a Ag-free tape, MgB₂ phase was formed as a main phase by reaction at 500°C for 24 h as shown in the top XRD pattern. However, a Ag-free tape prepared in a different batch contained a large amount of unreacted Mg as shown in the middle pattern of Fig. 3. On the other hand, Ag-added tapes composed of almost single MgB₂ phase were obtained by the low temperature reaction under the same conditions with high reproducibility. As clearly seen in Fig. 3, the diffraction peaks of the Ag-added tape are sharp compared to that of Ag-free tape. Superconducting transition of the Ag-added tape is also sharper than that of the Ag-free tape, while their $T_{\text{onset}}$ were almost identical being ~36 K as shown in Fig. 4. These suggested that the small amount of Ag-addition improved crystallinity and connection of MgB₂ grains. Reflecting these effects by Ag-addition, Ag-added tapes exhibited a high $J_c$ of $\sim 3 \times 10^5$ A cm$^{-2}$ at 5 K in low fields, while that of the Ag-free tape was $\sim 2 \times 10^4$ A cm$^{-2}$.

3.2. Synthesis of a dense Ag-added MgB₂ bulk

Low temperature synthesis of a dense MgB₂ bulk was attempted by the PICT-diffusion method. A dense MgB₂ bulk with 5 mm in length was grown from the interface of a liquid of Mg+0.1Ag and a powder mixture of B and MgB₂ by heating at 700°C for 72 h, while high temperatures above 780°C was required for the diffusion reaction in our previous study on the Ag-free MgB₂ bulks [2,3]. Therefore, the Ag-addition was found to promote diffusion reaction of Mg. Density of this sample
was estimated to be ~90% of the theoretical density. Figure 5 shows a fractured surface of the Ag-added dense MgB$_2$ bulk. Relatively large MgB$_2$ crystals with several µm were densely packed in the bulk. As shown in Fig. 4, $T_c$ of the dense bulk was slightly low ~38 K, suggesting that a small amount of Ag substituted for Mg as reported by Chen et al. [18]. Corresponding to the improvement in density, this bulk showed high $J_c$ characteristics as shown in Fig. 6. Further enhancement of $J_c$ can be expected by optimizations of the addition level of Ag and heating conditions.

![Figure 5](image5.png)  
**Figure 5.** Secondary electron image of fractured surface of a Ag-added MgB$_2$ bulk prepared by the PICT-diffusion method at 700°C for 72 h.

![Figure 6](image6.png)  
**Figure 6.** ZFC magnetization curve of Ag-added MgB$_2$ bulk prepared by the PICT-diffusion method. The inset shows its $J_c$-$H$ curve at 20 K.

### 4. Conclusions
Effects of Ag-addition on the low temperature phase formation of MgB$_2$ bulks and tapes were studied. Including a SiC-added sample, MgB$_2$ bulks with high phase purity were successfully obtained by heat-treatment done at 550°C for 72 h. A SiC added-sample showed higher $J_c$ under high fields at 20 K than that of a SiC-free sample. In the fabrication of “in-situ” Fe-sheathed tape by heating at 500°C for 24 h, the Ag-addition was found to improve crystallinity and coupling of MgB$_2$ grains, resulting in a relatively high $J_c$. In addition, a highly dense MgB$_2$ bulk with high $J_c$ was obtained by the diffusion reaction of Mg+0.1Ag(liquid) into a pressed powder mixture of 2B+ MgB$_2$ at 700°C.

All above results suggested that the small amount of Ag-addition, which enhances the reactivity of Mg, is universally effective for decreasing the synthesis temperature of MgB$_2$ bulks and tapes. Additional investigations on the optimization of synthesis procedures will provide low temperature processed MgB$_2$ bulks and tapes with excellent $J_c$ characteristics enough for various practical applications.

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