Enhanced $J_c$ of B-rich and SiC doped MgB$_2$ tapes fabricated by a modified in-situ PIT method with two stage heat treatment

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Abstract. B-rich and SiC doped MgB$_2$ tapes were fabricated by a modified in-situ PIT method with two stage heat treatment. B composition ratio and an amount of SiC doping were systematically changed. The effect of pre-heating and final heating conditions on $J_c$-$B$ properties was also studied. Mean grain size of MgB$_{2.8}$ specimens reduced to about 100 nm by increasing SiC doping 5.7%. In low fields $J_c$ slightly increased for a little SiC doped specimens. On the other hand, in high fields $J_c$ obviously increased with increasing SiC doping. Maximum $J_c$ reached $1.8 \times 10^3$ A/cm$^2$ at 3 T, 20 K for MgB$_{2.8}$ specimen doped SiC 5.7 mol%. $B_{irr}$ also increased with increasing SiC doping. $J_c$ systematically increased with the decrease of temperature of pre-heat treatment. In contrast $J_c$ systematically increased with the increase of temperature of final heat treatment. Best $J_c$ of $8.6 \times 10^4$ A/cm$^2$ at 20 K, 0 T was achieved for specimen with 700 °C for 5 hours + 800 °C for 1 hour heating. $B_{irr}$ tended to increase with the increase of $J_c$.

1. Introduction

A metallic “high-$T_c$” superconductor MgB$_2$ has attracted a great deal of interest in its practical applications at relatively high temperature of 15-20 K, which is possible to be operated by liquid hydrogen or low loading cryocoolers. Most important features of MgB$_2$ superconductors are having a strong inter grain connectivity due to its long coherence length and a strong pinning potential due to its large condensation energy density even at high temperature [1]. Previous studies revealed that the dominant pinning centers of MgB$_2$ are grain boundaries [2, 3]. However it is not easy to control the grain size by only heat treatment [4]. Dou achieved $J_c$ enhancement by SiC nano-particle doping into MgB$_2$ [5]. It is explained that C substitution on B sites deteriorates the crystallinity of MgB$_2$ grains, resulting in an enhancement of grain boundary pinning, $f_{GB}$ [6, 7]. However, coincidentally it causes the degradation of $T_c$, therefore $J_c$ at high temperature under high fields is not still enough for practical use. Recently, we have fabricated B-rich MgB$_2$ tapes for the purpose of introducing non-reacted B and secondary phases into grain boundaries as incremental flux pinning centers, resulting in a significant improvement of $J_c$ with increase of B composition ratio without $T_c$ degradation [8]. Analyses based on the grain boundary pinning theory revealed that the origin of $J_c$ enhancement comes from both increase of grain boundary density due to suppression of grain growth in Mg poor condition and an enhancement of $f_{GB}$ due to the existence of non-superconducting phases. We have also studied the
difference of flux pinning characteristics between SiC doped and B-rich MgB\(_2\) tapes and pointed out that the difference arose from the different flux pinning mechanism \[9\].

In this study, for further improvement of \(J_c\)-B properties of MgB\(_2\) tapes, B-rich and SiC doped MgB\(_2\) tapes were fabricated by a modified in-situ PIT method with two stage heat treatment. B composition ratio and an amount of SiC doping for MgB\(_2\) tapes were systematically changed. The pre-heating and final heating conditions were also methodically changed. Superconducting properties of such MgB\(_2\) tapes are investigated by magnetic measurements.

2. Experimental details

MgB\(_2\) tapes were prepared by a modified PIT method \[10\]. Mg powder (200 mesh, 99.9% purity), amorphous Boron (325 mesh, 99% purity) and SiC nano-particles (50 nm) were used as starting materials. The mixed powder with various composition ratio was filled in stainless steel (SUS 316) tubes with outer diameter of 6.0 mm, inner diameter of 4.0 mm and length of 60.0 mm. Its both ends were perfectly sealed by Cu stopples. They were deformed to rectangular rods with outer side of 3.8 mm by a groove-rolling machine. The rectangular rods were pre-heated at 700-800 °C for 5 hours to synthesize MgB\(_2\) grains in Ar atmosphere. Then the rods were flat-rolled into tapes with a thickness of 0.5 mm. Finally, the tapes were heat-treated at 600-800 °C for an hour in Ar. The specification of the MgB\(_2\) tapes is shown in table 1.

Phase identification of the specimens was investigated by a powder X-ray diffraction (XRD). Microstructure of flat surface of peeled MgB\(_2\) cores was observed by both an optical microscope and a scanning electron microscope (SEM). Magnetization was measured by a SQUID magnetometer at various temperature and magnetic fields perpendicular to the tape surface. \(T_c\) was defined as the temperature at which the magnetization changed from a diamagnetic to a paramagnetic state. \(J_c\)-B curves were evaluated from the width of the magnetic hysteresis using the extended Bean model. Irreversibility field \(B_{irr}\) was defined by a criterion of \(J_c = 100\) A/cm\(^2\).

Table 1. Specification of the specimens

| Specimen No. | Compositions Ratio(mol) | 1st Heat Treatment | 2nd Heat Treatment | SiC dope(mol%) | \(T_c\) | \(B_{irr}\) at 20 K |
|--------------|------------------------|-------------------|-------------------|---------------|------|-------------------|
| S1 1.0 2.8   | 800 °C-5 h             | 800 °C-1 h        | 0.0               | 38 K          | 3.2 T|
| S2 1.0 2.8   | 800 °C-5 h             | 800 °C-1 h        | 2.9               | 36 K          | 3.7 T|
| S3 1.0 2.8   | 800 °C-5 h             | 800 °C-1 h        | 5.7               | 35 K          | 3.9 T|
| S4 1.0 2.8   | 800 °C-5 h             | 800 °C-1 h        | 8.6               | 35 K          | 2.9 T|
| S5 1.0 2.8   | 800 °C-5 h             | 800 °C-1 h        | 11                | 34 K          | 3.4 T|
| B1 1.0 2.2   | 800 °C-5 h             | 800 °C-1 h        | 5.7               | 35 K          | 3.5 T|
| B2 1.0 2.6   | 800 °C-5 h             | 800 °C-1 h        | 5.7               | 35 K          | 3.8 T|
| H1 1.0 2.6   | 800 °C-5 h             | 700 °C-1 h        | 5.7               | 35 K          | 3.2 T|
| H2 1.0 2.6   | 800 °C-5 h             | 600 °C-1 h        | 5.7               | 35 K          | 1.7 T|
| H3 1.0 2.6   | 700 °C-5 h             | 800 °C-1 h        | 5.7               | 35 K          | 3.7 T|
| H4 1.0 2.6   | 700 °C-5 h             | 700 °C-1 h        | 5.7               | 35 K          | 3.7 T|
| H5 1.0 2.6   | 700 °C-5 h             | 600 °C-1 h        | 5.7               | 35 K          | 2.4 T|

3. Flux pinning model

Flux pinning models based on our recent studies for various MgB\(_2\) tapes fabricated by the modified PIT method with two stage heat treatment are schematized in figure 1. Figure 1-a shows the standard
model for stoichiometric MgB$_2$ tapes. The main pinning centers are grain boundaries. Figure 1-b shows the model for B-rich specimens. Grain boundary density increases due to the suppression of grain growth in Mg poor condition. In addition, the grain boundary pinning $f_{GB}$ enhances due to the existence of a moderate amount of non-superconducting phases. Excellent $J_c$-B performance of $8.4 \times 10^5$ A/cm$^2$ at 20 K under 3 T was obtained for MgB$_{2.8}$ specimen [9].

On the other hand, the model for SiC doped MgB$_2$ tapes is indicated in figure 1-c. Previous works reveals that C substitution on B sites deteriorates crystalline of MgB$_2$ grains, resulting in an enhancement of $f_{GB}$ and $B_{in}$[6, 7]. However, coincidentally the degradation of $T_c$ and the existence of Mg$_2$Si phases which may interrupt current transport between grains are becoming real and substantive problem.

In this study we are exploring the possibility of further improvement of the flux pinning properties for MgB$_2$ tapes by combining those two methods.

**Figure 1.** Flux pinning model of B-rich and SiC doped MgB$_2$ tapes.

4. Result and discussion

4.1. $J_c$-B properties for SiC doped specimens

The dominant phase of XRD peaks for all specimens was MgB$_2$. MgB$_4$ and other possible B compounds were hardly detected, that was similarly reported by Xu et al. [11]. However, they confirmed the existence of MgB$_4$ nanoparticles by TEM studies. Therefore, there is a high possibility that such phases exist in our B-rich specimens. For SiC doped specimens Mg$_2$Si peaks were slightly observed.

Figure 2 shows typical SEM images of flat surface of tape specimens. SEM studies showed that the grain size tended to be smaller with the increase of SiC doping level. Mean grain size of S1, S3, S5, B1 and B2 specimens was 400 nm, 100 nm, 150 nm 125 nm and 100 nm respectively.

$T_c$ decreased with the increase of SiC doping level. $T_c$ considerably decreased to 34 K for S5 specimen.

$J_c$-B curves at 20 K for various SiC doped specimens were shown in figure 3. Non-doped B-rich S1 specimen indicated a high $J_c$ of $7.1 \times 10^4$ A/cm$^2$ at 0 T, but $J_c$ rapidly decreased in high fields. In low fields $J_c$ slightly increased for a little SiC doped specimens. Maximum $J_c$ of $7.2 \times 10^4$ A/cm$^2$ was obtained for S2 specimen at 0 T.
On the other hand, in high fields, $J_c$ obviously increased with increasing SiC doping. Maximum $J_c$ reached $1.8 \times 10^3 \text{A/cm}^2$ at 3 T for S3 specimen with smallest grain size. $B_{irr}$ also increased with increasing SiC doping. The maximum value of 3.9 T at 20 K was derived for S3 specimen.

Based on our flux pinning model, enhancement of $f_{GB}$ resulted in slight increase of $J_c$ in low field. On the other hand, increase of $J_c$ in high field was thought to be due to improvement of $B_{irr}$. Decrease in $J_c$ for S4 and S5 specimens was thought to be caused by the existence of Mg$_2$Si phase.

**Figure 2.** Typical SEM images of the tape specimens (A-S1, B-S3, C-S5, D-B1 and E-B2).

**Figure 3.** $J_c$-B curves at 20 K for various SiC doped specimens.

4.2. $J_c$-B properties for optimized B-rich and SiC doped specimens

Based on the above result, the effect of B composition ratio on $J_c$-B curves for 5.7% SiC doped specimens was studied. By SEM observation the grain size of each specimen hardly changed. Figure 4 shows $J_c$-B curves for 5.7% SiC doped specimens with various B composition ratio. Maximum $J_c$ of $7.6 \times 10^4 \text{A/cm}^2$ at 20 K, 0 T was obtained for B1 specimen. On the other hand, $J_c$ increased with increasing B composition ratio in high fields. The maximum $J_c$ was $1.8 \times 10^3 \text{A/cm}^2$ for S3 specimen.

4.3. Effect of heat treatment on $J_c$-B properties for B-rich and SiC doped specimens
Finally, we studied the effect of various heat treatment conditions on $J_c$-$B$ properties for the sample as B2 specimen with superior high-field performance at 20 K. Figure 5 shows $J_c$-$B$ curves at 20 K for specimens with various heat treatment conditions. $J_c$ systematically increased with the decrease of temperature of pre-heat treatment and $J_c$ systematically increased with increase of temperature of final heat treatment notably in low field. Best $J_c$ of $8.6 \times 10^4$ A/cm$^2$ at 20 K, 0 T was achieved for specimen H3. $B_{irr}$ tended to increase with the increase of $J_c$. The maximum value of 3.7 T at 20 K was derived for H3 specimen.

Figure 4. Effect of B composition ratio on $J_c$-$B$ properties for 5.7 % SiC doped specimens.

Figure 5. The effect of various heat treatment conditions on $J_c$-$B$ properties for B2.
5. Conclusion

For further improvement of $J_c$-B properties of MgB$_2$ tapes, SiC doped B-rich MgB$_2$ tapes were fabricated by a modified in-situ PIT method with two stage heat treatment. B composition ratio and an amount of SiC doping for MgB$_2$ tapes were systematically changed. The pre-heating and final heating conditions were also methodically changed. SEM studies revealed that the grain size tended to be smaller with the increase of SiC doping level. In low fields $J_c$ slightly increased for a little SiC doped specimens. On the other hand, in high fields, $J_c$ obviously increased with increasing SiC doping. Maximum $J_c$ reached $1.8 \times 10^3$ A/cm$^2$ at 3 T, 20 K for MgB$_{2.8}$ specimen doped SiC 5.7 mol%. $B_{irr}$ also increased with increasing SiC doping. $J_c$ systematically increased with the decrease of temperature of pre-heat treatment and $J_c$ systematically increased with the increase of temperature of final heat treatment. Best $J_c$ of $8.6 \times 10^4$ A/cm$^2$ at 20 K, 0 T was achieved for specimen with 700 °C for 5 hours + 800 °C for 1 hour heating. $B_{irr}$ tended to increase with the increase of $J_c$.

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