The performance improvement of MgB₂ prepared by the Mg diffusion method with the MgB₄ addition

H Zhang¹, L Li ¹, Y Zhao¹², Y Zhang¹

¹Key Laboratory of Maglev Train and Maglev Technology of Ministry of Education, Superconductivity and New Energy R&D Center, Southwest Jiaotong University, Chengdu 610031, China,
²School of Physical Science and Technology, Southwest Jiaotong University, Chengdu 610031, China

zhanghong@home.swjtu.edu.cn

Abstract. The Mg diffusion method with the MgB₄ addition is carried out to improve the MgB₂ application performance. The precursor B powders and MgB₄ powders are uniformly mixed as the ratio of \((1-4x) : x \text{ mol } \%\), \((x = 0, 1, 2, 5, 10 \text{ and } 20)\). The mixed powders are pressed into bulks and the excess of Mg powders are added into the iron pipe. Then the heat treatment is carried out under the pure argon atmosphere. Finally, the high-quality MgB₂ bulks are achieved with high density. The superconducting critical temperature of the MgB₂ bulks decreases slightly with the increase of MgB₄ addition content. However, the critical current density increases significantly at the high-fields. It is perhaps due to the small-sized MgB₄ impurities in MgB₂ bulk function as effective pinning centers and generates significant lattice distortion in the MgB₂ lattice to yield improved \(J_c\) performance in the applied field. It suggests that further improvement in the superconducting properties of the MgB₂ added with the MgB₄ will be possible via a better control of the composition and processing parameters. This also provides a reference for improving the preparation of MgB₂ wire.

1. Introduction

High critical current density and high irreversible field of the MgB₂ is one of the keys to the large-scale application of MgB₂. Because these properties are very sensitive to preparation conditions, a large amount of research about MgB₂ preparation conditions were reports[1~4], but there are still no optimal results. Although the commonly used method of solid state reaction is simple, high porosity is one of the important factors that limit the current transport capacity of MgB₂ materials[5]. On the other hand, Mg is a kind of material which can be very easy to be oxidized and will inevitably bring oxygen into the raw material during the preparation of MgB₂ by solid state reaction. Accumulation of MgO in
the MgB$_2$ grain boundary leads to a decrease in the $J_c$ value of MgB$_2$[6]. Several reports indicating that the diffusion method[7–9] can avoid void formation in the MgB$_2$ and is effective in forming high-density MgB$_2$. By a theoretical calculation, the density of MgB$_2$ materials prepared by diffusion method can reach 100% of the theoretical density of MgB$_2$. At present, the density of MgB$_2$ wire prepared by diffusion method has reached more than 95% of MgB$_2$ theoretical density in the laboratory[10]. At the same time, Mg diffusion into B materials and forming a dense MgB$_2$ at the interface can effectively prevent MgO from getting into the MgB$_2$ superconductor and the purity of MgB$_2$ sample is improved. Therefore, the MgB$_2$ current transport capacity is effectively improve by the diffusion method preparation.

However, the critical current density of the wire prepared by the diffusion method is still decreasing very fast at high magnetic fields, and the methods of element doping are needed to improve the critical current density at high magnetic fields[11,12]. Other impurity elements are usually introduced into the MgB$_2$ to enhance the flux pinning but reduce the superconductivity of MgB$_2$. So the doping amount is limited.

MgB$_4$ addition is introduced in this paper, which can avoid the introduction of other elements in to the MgB$_2$. Also, MgB$_4$ as the precursor of the MgB$_2$ forming reaction can promote the formation of MgB$_2$. At the same time, it is reported that the small self-generated coherent MgB$_4$ particles trapped in the MgB$_2$ can be used as an effective pinning center to improve the critical current density of the MgB$_2$ [13]. Therefore, in this paper, a certain amount of MgB$_4$ is added in to the precursor to prepare the MgB$_2$ by the diffusion method, which can artificially control the amount of MgB$_4$ in the MgB$_2$ and provide references to the actual production process.

2. Experiments

MgB$_4$ are prepared by in-situ solid-state reaction between Mg (99.99%) and B (99.9%) in the nominal stoichiometry of Mg:B = 1:4. They are mixed and ground, followed by pelletization. A high temperature is required to synthesize MgB$_4$ and an attempt has been done in the temperature 1050°C. Due to the high sintering temperature, a large amount of MgO is formed in those samples. In order to remove the MgO, acid washed is performed and a “cleaner” sample of MgB$_4$ is obtained.

MgB$_2$ bulks samples are prepared by an Mg diffusion method. B powder (purity >99.9% amorphous) and a amount of MgB$_4$ are mixed with the ratio (1-4x) : x, (x = 0,1mol%, 2mol%, 5mol%, 10mol% and 20mol%, respectively) . The well-mixed powders are pressed into bulks with the diameter of 10 mm and the thickness of about 1 mm under a pressure of ~20MPa. The bulks are sealed in the stainless steel tube which filling with amount of Mg powder and put into furnace for heating to 700 °C for 5 hours. Then the furnace cools to room temperature.

The sample microstructure, crystal structure and phase composition are analyzed by the scanning electron microscopy (SEM) and X-ray diffraction (XRD). The superconducting transition and magnetic hysteric loop are measured by Quantum-Design SQUID XL. The $J_c$ values of the MgB$_2$ slices are determined using Bean critical state model: $J_c = 20 \times (\Delta M) / [(a(1-a/3b)]$ with $a$, $b$ ($a \leq b$) being the edge lengths of a thin sheet in the plane. $T_c$ is defined as the onset temperature at which diamagnetic properties are observed.

3. Results and discussion

Figure 1 shows the typical X-ray diffraction $\theta$-2$\theta$ patterns of MgB$_4$ powders which before and after acid leaching. MgB$_4$ appears as a primary phase with MgO as the secondary phase. The high sintering temperature in prolonged time produced a relatively larger amount of MgO and this was inevitable due to the presence of residual O during the sintering[14]. The MgO impurity was then removed by immersing the samples in HNO$_3$ solution for 5 minutes. As shown in figure 1, the peaks of MgO were reduced to a much lower intensity. Thus, a “cleaner” sample of MgB$_4$ was obtained and can be used later for synthesizing MgB$_2$.

Figure 2 shows the typical $\theta$-2$\theta$ X-ray diffraction patterns of MgB$_2$ with the various MgB$_4$ addition contents of 0 to 20 mol%. In addition to the diffraction peaks of MgB$_2$, the diffraction peaks of MgB$_4$, 

\[ 3 \times \Delta I = \mu_0 \times \pi \times r^2 \times \Delta \theta \]

\[ \mu_0 \times \pi \times r^2 \times \Delta \theta = \Delta I \times \mu_0 \times S \times \Delta \theta \]

\[ S = \frac{\Delta I}{\mu_0 \times \pi \times r^2 \times \Delta \theta} \]
MgO and pure Mg are also can be detected as shown in figure 2. The pure Mg presents because of the magnesium residues in the bulk during the liquid magnesium diffusion into the bulk.

Figure 1. Typical X-ray diffraction θ-2θ patterns of MgB$_4$ powders which before and after acid leaching.

Figure 2. Typical X-ray diffraction θ-2θ patterns of MgB$_2$ samples with the various MgB$_4$ addition of: (A0) 0; (A1) 1 mol %; (A2) 2 mol %; (A5) 5 mol %; (A10) 10 mol %; (A20) 20 mol %.

Table 1. The relative content of MgB$_4$ and MgO in the MgB$_2$ bulk

| the relative content (mol%) | A0  | A1  | A2  | A5  | A10 | A20 |
|-----------------------------|-----|-----|-----|-----|-----|-----|
| $\frac{I_{\text{MgB}_4(121)}}{100\%}$ | 0   | 4.28| 10.10| 14.11| 7.58| 8.02|
| $\frac{I_{\text{MgB}_4(121)} + I_{\text{MgB}_2(101)}}{100\%}$ | 4.75| 5.36| 11.47| 10.38| 5.69| 7.16|

The relative contents of MgB$_4$ and MgO in the MgB$_2$ bulk are calculated from the intensity value of M (M are MgB$_4$(121) and MgO(220), respectively) and MgB$_2$(101) diffraction peaks by the expression: $I_M/(I_{\text{MgB}_4(121)} + I_{\text{MgB}_2(101)})$. Table 1 show the relative contents of MgB$_4$ and MgO in the MgB$_2$ bulk which prepared with the various MgB$_4$ addition of 0 to 20 mol%. As shown in table 1, the relative MgO contents in the MgB$_2$ samples prepared with the MgB$_4$ addition are more than that of the samples prepared without the MgB$_4$ addition. It seems that the addition of MgB$_4$ introduced the MgO into the MgB$_2$ bulk. This could be due to a small portion of MgO which the MgB$_4$ precursor contains and a little amount of MgO comes from the outside of the precursor bulk. At the same time, the presence of MgB$_4$ in the MgB$_2$ bulk suggests that MgB$_4$ does not fully participate in the reaction of the MgB$_2$ formation.

Figure 3 shows scanning electron microscope (SEM) images of the MgB$_2$ samples with the various MgB$_4$ addition of 0 to 20 mol%. All the samples show the high density and uniform characteristic. It is means that the diffusion process is effective in achieving higher-density MgB$_2$. 


Figure 3. Scanning electron microscope (SEM) images of MgB$_2$ samples with various MgB$_4$ addition of: (a) 0; (b) 1 mol %; (c) 2 mol%; (d) 5 mol%; (e) 10 mol%; (f) 20 mol%.

Figure 4. Normalized magnetization versus temperature curve of the MgB$_2$ samples with various MgB$_4$ addition of: (0) 0; (1) 1 mol%; (2) 2 mol%; (5) 5 mol%; (10) 10 mol%; (20) 20 mol%. Insert is the superconducting critical temperature as a function of MgB$_4$ addition content.

Figure 4 shows normalized magnetization versus temperature curve of the MgB$_2$ samples with various MgB$_4$ addition of 0 to 20 mol%. Inserted is the superconducting critical temperature as a function of MgB$_4$ addition content. It can be seen that the $T_c$ decreases slightly with the precursor MgB$_4$ addition content increasing. The $T_c$ decreasing in this work may be due to the impurity phase existences of MgB$_4$ and MgO in the MgB$_2$ samples as shown in the figure 2.

Figure 5 shows the magnetic critical current density ($J_c$) versus the magnetic field of the MgB$_2$ samples with various MgB$_4$ additions at different temperatures. The various MgB$_4$ additions are 0 to 20 mol % and the temperature is 10 K to 20 K. It is noted that the $J_c$ of the MgB$_2$ decreases with the precursor MgB$_4$ addition at low-fields compared with that of the MgB$_2$ sample without the precursor MgB$_4$ addition. However, the $J_c$ increases with MgB$_4$ addition at high-fields and the 5 mol% MgB$_4$ addition sample has the highest $J_c$ value. The enhancement of $J_c$ value at the high-fields is perhaps due
to the small-sized MgB₄ impurities in MgB₂ bulk prepared by Mg diffusion method. The MgB₄ impurities has been observed to function as effective pinning centers and generate significant lattice distortion in the MgB₂ lattice to yield improved \( J_c \) performance in the applied field[13]. When the MgB₄ addition content more than 5 mol%, the \( J_c \) value decrease perhaps due to more precursor MgB₄ contribute into the formation reaction of the MgB₂ which leads to the reduction of the final MgB₄ remaining amount in the MgB₂ as shown in the table 1. To verify the improved flux pinning in the MgB₂ material added by MgB₄, micro-structural experiments are necessary. This study is under the way. It suggests that further improvements in the superconducting properties of the MgB₂ bulk added with the MgB₄ will be possible via a better control of the composition and processing parameters.

4. Summary
The high-quality MgB₂ bulks are achieved with high density by the Mg diffusion method. The superconducting critical temperature decreases slightly with the increase of precursor MgB₄ addition. However, the critical current density increases significantly at the high-fields. It suggest that further improvement in the superconducting properties of the MgB₂ bulk added with the MgB₄ will be possible via a better control of the composition and processing parameters.

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