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Preparing MgB₂ With Excessive Mg Environment Sintering and Two-Step Sintering Approach

Sihai Zhou, Yun Zhang, Alexey V. Pan, Shixue Dou, Koochae Chung, and Jaimoo Yoo

Abstract—MgB₂ superconductors were made with two processes in this work. In one case, the SiC doped MgB₂ pellets were sintered in excessive Mg medium. It is found that the samples sintered in excessive Mg medium present Mg-rich composition comparing with the one sintered in Ar gas. The density is higher and the resistance is lower due to the penetration of Mg into the pores and grain boundary of MgB₂, which is beneficial to the Jc improvement. In the other case, a two-step process was employed to make MgB₂. Jc of the sample with the composition of MgB₂ is very low after the first sintering. The Jc was dramatically improved after the second sintering, but Jc of the two-step made sample is still poorer than the MgB₂ made with general one step sintering due to the connectivity deterioration caused by the pulverization prior to the second sintering.

Index Terms—Critical current density, MgB₂, SiC doping, superconductor.

I. INTRODUCTION

SUPERCONDUCTIVITY of MgB₂ was found in 2001 [1]. MgB₂ has a Tc of 39 K, higher than that of low temperature superconductors. It presents no weaklink problem between grain boundaries in comparison with the high-temperature superconductor [2]. The raw materials of this superconductor are cheaper than Nb, Ti of low temperature superconductor. Fe can be used as sheath material, which is much cheaper than Ag that is used for Bi2223 tapes. Its relatively high Tc enables the applications at above 20 K with a cryogen-free cryo-cooler. Most of the MgB₂ superconductors are made with the so called “in-situ” method. In this method, Mg and B powders are mixed, pressed and sintered at a temperature of 650–900°C [3]–[7].

The advantages of the “in-situ” method are cheap fabrication, high Jc and flexibility of doping the MgB₂ with other elements. However, this method has a disadvantage in that there are voids, cracks in the precursor pellets even before the sintering. During the sintering, the Mg will melt or evaporate and react with B, leaving holes after the reaction. The MgB₂ volume shrink and cause even more holes, the overall density of the resultant MgB₂ is only half of the theoretical density. The low density of the MgB₂ wire lead to less supercurrent flowing area, to improve the density is a possible way to improve the Jc [8].

When the Mg + 2B precursor pellets are sintered under protective Ar, there is a possibility that the Mg evaporates into the environment and cause Mg insufficiency. There is also the other possibility that O₂ in the environment reacts with MgB₂ and form MgO or B₂O₃ impurities thus damages the superconductivity. It is expected that sintering MgB₂ in a Mg excessive medium can prevent Mg from evaporated away or oxidized, the excessive Mg from outside the pellets may penetrate into the MgB₂ and produce Mg-rich MgB₂ and improve the grain connectivity thus achieve higher Jc.

In the first part of this paper, SiC doped MgB₂ were sintered under the protection of excessive Mg environment. The microstructure and Jc were studied.

A two-step fabrication is another attempt to fabricate higher density MgB₂. In this fabrication, Mg + 4B are prepared first, and more Mg is added into MgB₂, pressed and then sintered at a higher temperature as the second step. By this way, the holes resulting from the first step sintering can be erased, so the final density can be higher. The second task of this paper dealt with the effects of the two-step sintering on Jc.

II. EXPERIMENTAL DETAILS

A. Sample Preparation

1) SiC Doped MgB₂ Sintered in Excessive Mg Medium: In this experiment, 10 wt% SiC powder was added in Mg (90%) + 2B (99%) powder and mixed with mortar and pestle by hand for 0.5 h. The particle size for the SiC powder is 30 nm, boron powder is 100 nm and the Mg powder is 11 μm. The mixed powders were pressed into pellets of diameters of 13 mm with a pressure of 7.5 GPa. The pressed pellets were buried in Mg turnings and then sealed in iron tubes to prevent O₂ getting in during the sintering. The sintering temperature was 800°C, sintered for 1 h in flowing Ar. A reference sample was also made in the same time but sintered in high purity Ar gas.

2) Two-Step Sintering to Make MgB₂: In this case, Mg + 4B powders were mixed, pressed, and sintered at 800°C as the first step. The obtained MgB₁₄ samples were pulverized and ground into fine powder. Mg powder was added to achieve the MgB₂ composition. The Mg added powders were then mixed, pressed, and sintered at 850°C under Ar protection.

B. Characterization

The obtained pellets were characterized with a PW1730 X-Ray Diffraction (XRD) with Cu Kα radiation being used. Scanning Electronic Microscopy (SEM) was used to study their...
III. RESULTS AND DISCUSSION

A. SiC-Doped MgB$_2$ Sintered in Excessive Mg Medium

The $T_c$ of the SiC-doped samples is shown in Fig. 1 together with the $T_c$ of an MgB$_2$ sample sintered in Ar gas with the same sintering procedure. The $T_c$ of the SiC-doped sample is about 34.7 K. The drop of the $T_c$ is caused by the carbon originating from SiC doping, which was discussed in our previous work [10]. The sample sintered in excessive Mg has wider transition breadth; this is understood to be caused by the composition variety of the excessive Mg treated sample.

Fig. 2 depicts the $J_c$ of the two SiC-doped samples, an undoped MgB$_2$ was included as reference. Both SiC-doped samples have improved $J_c$ at higher field than the undoped MgB$_2$. The sample sintered in Mg wrap has slightly higher $J_c$ as comparing with the one sintered in Ar gas. The $J_c$ improvement probably is due to the denser microstructure and better connectivity. The resistance of the two samples was measured and the results are shown in Table I, sintering in excessive Mg have decreased sample’s resistance at both 300 K and 40 K. It should be the result of Mg filtrating into the MgB$_2$, healing some cracks. The free Mg’s presence is also a factor for the resistance decrease. The effect of the sintering in Mg on $H_{c2}$ can be seen in Fig. 3, the Mg-treated sample has higher $H_{c2}$.

XRD were used to analyze the phase composition. Fig. 4 is the XRD of the SiC doped MgB$_2$ samples sintered in different environment. In both samples, there were MgB$_2$, Mg$_2$Si and MgO. The sample sintered in Mg medium showed significant Mg peaks and weaker MgO peak comparing with the Ar sintered sample. The SEM pictures are depicted in Fig. 5. At lower magnification, there is no obvious difference between the Ar sintered sample and Mg sintered sample. However, at higher magnification, the Mg sintered samples show much dense microstructure, it seems that the Mg penetrated inside the small gaps between the MgB$_2$ grains. This result is in consistent with the lower resistance of this sample, and also confirmed by the XRD results. The mass density of the Mg sintered sample is 1.5 g/cm$^3$, higher than that of the Ar sintered one (1.3 g/cm$^3$). The density increased by 15%, the $J_c$ was also improved modestly. The $J_c$ improvement can be attributed to the connectivity improvement due to the Mg penetration.

B. MgB$_2$ Prepared Using the Two-Step Method

This method consists of two steps: firstly the pellets with Mg + dB composition were sintered at 800°C for 0.5 hrs. The obtained pellets were pulverized and Mg was added to reach MgB$_2$ composition. The XRD pattern for these two steps is presented in Fig. 6. The first step sintered sample presented MgB$_2$, MgB$_3$ and MgO phases. After the second step, MgB$_2$ phase become the dominating phase, only small percentage of MgB$_4$ and...
Fig. 4. XRD pattern for SiC doped MgB₂ sintered in different atmosphere.

Fig. 5. FESEM images for SiC doped MgB₂ sintered in different atmosphere (a) MgB₂ sintered in Mg excessive medium (b) sintered in Ar.

Fig. 6. XRD of the samples sintered for the first time and for the second time.

MgO remains. The ratio of MgO peak to MgB₂ peak decreased after the Mg addition, which is a hint that the MgO amount decreased after the Mg addition and second sintering.

The FESEM pictures for the first step and second step are shown in Fig. 7, an image for the one step made sample is also included for reference. It is seen that both the first step sintering and second sintering produced a porous structure. The second sintered sample shows denser structure comparing with the first sintered one. The mass density of the first sintered sample is 1.3 g/cm³, the density increase to 1.6 g/cm³ after the second sintering. The one step sintered sample shows similar porous structure, but its grain size is larger, and the connectivity between the grains looks better than that of the two-step sintered samples. It is obvious that the adding of Mg can improve the density, improve the Jc dramatically in the process of two-step sintering, comparing with the first step sintered sample.

The Tc for the first sintering and second sintering sample is shown in Fig. 8. The first sintering produced very wide transition width, a sign of multiple Tc phase existing or poor grain connectivity. After the second sintering, the Tc transition becomes very sharp, indicating better connectivity and more uniform phase composition. The Jc for the two samples is depicted in Fig. 9. It can be seen that the Jc of the second sintered sample increased dramatically in all fields both at 5 K and 20 K comparing with the one of the first sintered sample. However, even after the second sintering, the Jc of the two-step made sample is still one order of magnitude lower than the one of the one-step made samples. The possible reasons for the poor Jc is poor granular connectivity due to cracks and/or impurity at grain boundary.

The Jc result is consistent with the XRD and SEM result, indicates the two-step sintering method is not an effective way for improving Jc. In order to obtain high Jc, it is necessary to not only to increase the mass density of the sample but also to achieve good connectivity in the same time.

IV. CONCLUSIONS

Two methods have been used to make MgB₂ superconductors. One is to sinter the MgB₂ in an excessive Mg medium; the other one is to make MgB₂ with two-step method. To sinter MgB₂ in excessive Mg medium can improve connectivity indicated by the larger mass density, lower resistance of the sample both at 300 K and 40 K after sintering in Mg. The connectivity improvement has good effects on the Jc improvement evidenced by the higher Jc of the Mg medium treated sample. The two-step
sintering, however, has no improvement in $J_c$ over the sample made with general one-step method.

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