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ARTICLE

Effect of Carbon and SiC Doping on Microstructures of MgB_2 Bulks and Wires by a Two-Step Reaction Method

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Abstract: Carbon and SiC doped MgB_2 bulks and wires were fabricated by a two-step reaction method. The MgB_4 samples were sintered at 900 ℃ for 2 h in closed argon atmosphere, and then an appropriate amount of Mg powder was mixed with the ground MgB_4 powder to get MgB_2 green compacts, which were sintered at 750 ℃ for 2 h to get bulk samples or at 680 ℃ for 2 h to get wire samples in closed argon atmosphere. Carbon or SiC doped MgB_2 bulk samples were also prepared by conventional solid state sintering for comparison. The phase evolution and the microstructure of MgB_2 samples were characterized by means of X-ray diffraction (XRD) and scanning electron microscope (SEM). The SEM results indicate that the compactedness and the dopant distribution homogeneity of MgB_2 samples prepared by the two-step reaction method are improved obviously. The carbon doping can more effectively introduce the dopants into MgB_2 crystalline lattice and grain boundaries compared with SiC doping.

Key words: MgB_2; doping; phase evolution; sintering; two-step reaction

MgB_2 has been regarded as one of the most promising superconductors since its discovery in 2001 [1]. However, the applications of pure MgB_2 superconductor face serious obstacles due to its low upper critical magnetic field (H_{c2}) and irreversibility field (H_{irr}) [2]. Chemical doping is an effective way to improve the superconductivity of MgB_2, and the SiC and C are thought to be the effective dopants [3-5]. In general, the MgB_2 samples were prepared by conventional direct sintering of the mixed powders of Mg, B and dopants in previous experiments [6-11]. The prepared MgB_2 samples had a high porosity, which decreased the effectively carried current area and restricted the increase of current density of MgB_2 superconductors. The two-step reaction method can effectively introduce the dopants into the MgB_2 crystalline lattice, and therefore improve the upper critical field [12].

However, the phase evolution and the microstructure of MgB_2 samples prepared by the two-step reaction method have not been studied yet and compared clearly with that prepared by conventional solid state sintering. In the present work, the doping effect of C and SiC on the phase evolution and the microstructure of MgB_2 bulks and wires prepared by the two-step reaction method were studied.

1 Experiment

The starting powders for the present investigation were Mg powder, crystalline boron powder, amorphous carbon and nano SiC powders. The powders with a nominal atomic ratio of $MgB_{1.92}C_{0.08}$ or $MgB_{1.92}(SiC)_{0.08}$ were prepared by a two-step sintering method. In the first step, magnesium, boron and carbon or nano SiC powders were separately weighed according to the nominal atomic ratio of $MgB_{3.84}C_{0.16}$ (for sample A) or $MgB_{3.84}(SiC)_{0.16}$ (for sample A'), and then they were separately mixed and ground in an agate mortar for 30 min in a vacuum glove box in argon atmosphere. The two

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powder mixtures were separately pressed into green disks at a pressure of 10 MPa; afterward they were enveloped in a niobium foil and put into a horizontal tubular furnace. The disks were sintered at 900 ℃ for 2 h in closed argon atmosphere. After sintering, the samples were cooled naturally to get sintered sample A and sintered sample A'. In the second step, the sintered bulks were separately ground into powders by mechanical grinding and then separately mixed with an appropriate amount of Mg powder to get the $MgB_{1.92}C_{0.08}$ (for sample B) or $MgB_{1.92}(SiC)_{0.08}$ (for sample B') powders. A part of the powders were separately pressed into green disks at a pressure of 10 MPa, and then sintered at 750 ℃ for 2 h in closed argon atmosphere to get bulk sample B and bulk sample B'. $MgB_{1.92}C_{0.08}$ (sample C) or $MgB_{1.92}(SiC)_{0.08}$ (sample C') bulks were also prepared by conventional solid state sintering for comparison. Another $MgB_{1.92}C_{0.08}$ (for sample B) or $MgB_{1.92}(SiC)_{0.08}$ (for sample B') mixed powders were separately filled in Nb/Cu composite tubes, and then the filled composite tubes were drawn to 1 mm in diameter. There was no any annealing during the fabrication process. After cold deformation, the composite wires were cut and sintered at 680 ℃ for 2 h in closed argon atmosphere, and then furnace-cooled to room temperature to get wire sample B and wire sample B'.

The phase composition was identified by XRD with Cu-Kα radiation. Microstructure was examined on cross section of MgB_2 bulks and wires by SEM.

2 Results and Discussion

Fig.1 shows the XRD patterns of (a) $MgB_{3.84}C_{0.16}$ (sintered sample A), (b) $MgB_{1.92}C_{0.08}$ (bulk sample B) prepared by two-step reaction method and (c) $MgB_{1.92}C_{0.08}$ (bulk sample C) prepared by conventional solid state sintering. It can be seen from pattern (a) in Fig.1 that the MgB_2 is the main phase, and a great amount of MgB_4 is formed in the first sintering reaction step. It can be seen from pattern (b) in Fig.1 that MgB_4 phase fully disappears because the reaction between MgB_4 and Mg converts into MgB_2 during the second sintering reaction step. Some residual magnesium can be found in the sample B and C.

Fig.2 shows the SEM images of bulk sample B and bulk sample C. It can be seen that the micro-scale pores are formed in the bulk sample C due to the vacancy and evaporation of magnesium, and the porosity of bulk sample B is evidently lower than that of bulk sample C. The density of sample C is 1.05 g cm^{-3}, while the density of sample B is 1.36 g cm^{-3}. Nardelli et al calculated the theoretical density of MgB_2 prepared by the two-step reaction method, which was 2.25 g cm^{-3}, while the theoretical density of MgB_2 prepared by the conventional solid state sintering method was 2.01 g cm^{-3} [13]. An increase of the density due to the change of reaction route likely contributes to the increase of J_c, which has been proved by our previous work [14]. The carbon doping could effectively introduce the dopants into the MgB_2 crystalline lattice and

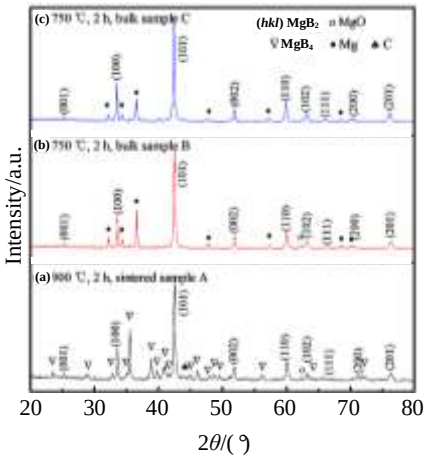

Fig.1 XRD patterns for sample A, B and C

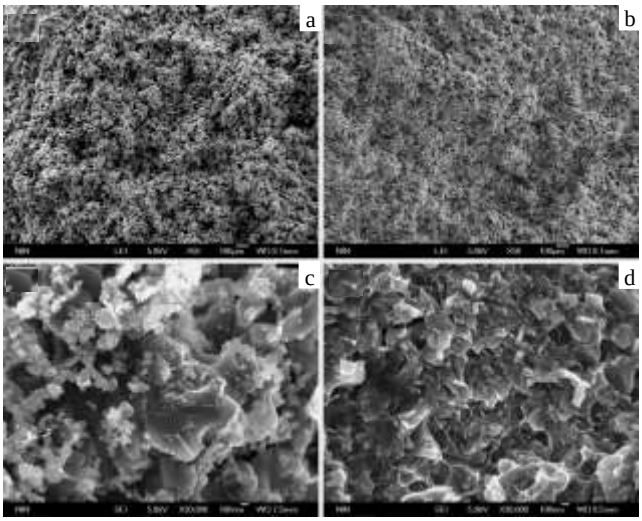

Fig.2 Typical SEM images for bulk sample B (a, c) and bulk sample C (b, d)

grain boundaries. Yan et al proved that the carbon atoms were uniformly distributed in the MgB_2 bulk prepared by the two-step reaction method [15]. According to the above-mentioned results the following finding can be drawn: the two-step reaction method can improve the compactedness and the dopant distribution homogeneity of MgB_2 sample compared with the conventional solid state sintering method.

Fig.3 shows XRD patterns of (a) $MgB_{3.84}(SiC)_{0.16}$ (sintered sample A'), (b) $MgB_{1.92}(SiC)_{0.08}$ (bulk sample B') prepared by two-step reaction method and (c) $MgB_{1.92}(SiC)_{0.08}$ (bulk sample C') prepared by conventional solid state sintering. It can be seen from pattern (a) in Fig.3 that MgB_2 is the main phase, and a great amount of MgB_4, some Mg_2Si and MgO are formed in the first sintering reaction step. It can be seen from pattern (b) and (c) in Fig.3 that MgB_4 phase also fully disappears. Some residual magnesium and Mg_2Si still can be found in bulk samples B' and C'.

Fig.4 shows SEM images of bulk sample B' and bulk

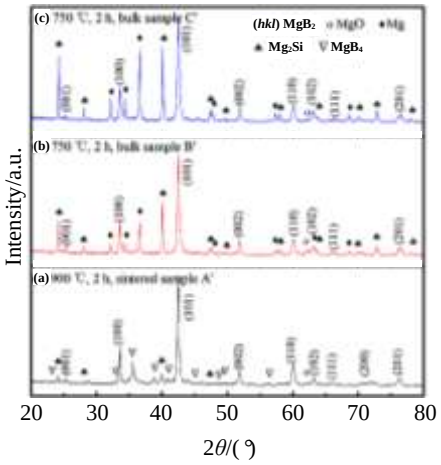

Fig.3 XRD patterns for sample A', B', and C'

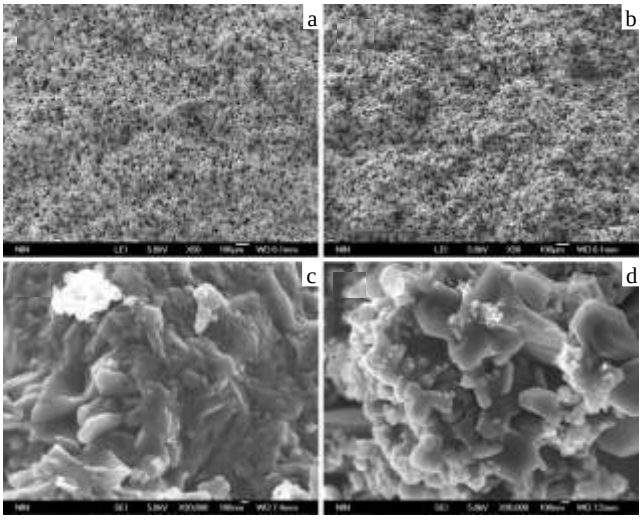

Fig.4 Typical SEM images for bulk sample B' (a, c) and bulk sample C' (b, d)

sample C'. It can be seen that the micro-scale pores are formed in bulk sample C' due to the vacancy and evaporation of magnesium, and the compactedness of bulk sample B' is better than that of bulk sample C'. The mechanism of SiC addition is that the nano-SiC reacts with Mg, resulting in releasing both highly reactive free C and by-products such as Mg_2Si [16]. The C enters the grains while Mg_2Si is expected to form at the grain boundaries, which may reduce the grain connection and thus impede the supercurrent [17]. From above discussion, it is clear that the two-step reaction method effectiveness to improve sample B' is basically same as that to improve sample B. However there is some difference, e.g., the grain connection of bulk sample B is better than that of bulk sample B'.

To further understand the phase evolution in MgB_2 prepared by the two-step reaction method, the microstructures of MgB_2 wire samples B and B' are shown in Fig.5. For fabrication of MgB_2 wires, however, the reaction route in ambient pressure

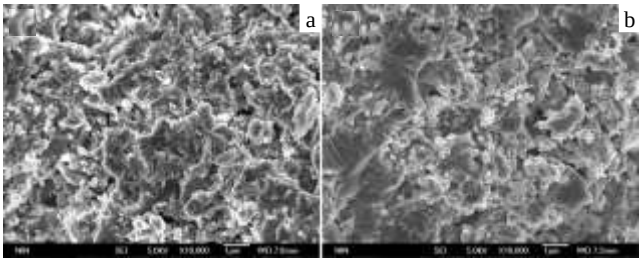

Fig.5 Typical SEM images for wire sample B (a) and wire sample B' (b)

to increase the density of sample is expected. The SEM observation shows that the SiC doping induces the worse grain connection because Mg_2Si is distributed at grain boundaries of MgB_2, so wire sample B has better grain connection than wire sample B'. It proves that the two-step reaction method is useful to fabricate dense MgB_2 wires.

3 Conclusions

1) Carbon and SiC doped MgB_2 bulks and wires can be fabricated by the two-step reaction method.

2) The two-step reaction method can effectively improve the compactedness and dopant distribution homogeneity of MgB_2 sample compared with conventional solid state sintering method.

3) The two-step reaction method is useful to fabricate dense MgB_2 wires.

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C 和 SiC 掺杂对分步反应法制备 MgB_2 块体和线材微观结构的影响

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摘　要：通过两步反应法制备了 C 和 SiC 掺杂的 MgB_2 块材和线材。首先，按一定比例均匀混合 Mg 粉、B 粉和 C 或 SiC 粉，压块后在 900 ℃密闭氩气条件下烧结 2 h，得到 C 或 SiC 掺杂的 MgB_4 块体；将一次烧结后的 MgB_4 块体磨碎过筛，和补充的 Mg 粉混合作为前驱粉末制备 MgB_2，MgB_2 块体在密闭氩气条件下 750 ℃烧结 2 h 而 MgB_2 线材在密闭氩气条件下 680 ℃烧结 2 h。同时采用传统的固态烧结法制备了 C 或 SiC 掺杂的 MgB_2 块体以作对比。对烧结后的样品进行了微观结构和相组成等分析检测。分步反应法与以往的固态烧结法相比，不仅因降低了 Mg 元素的影响而提高样品组织致密性，更因其采用了分步混合粉末而大大地提高了元素掺杂的均匀性。和 SiC 掺杂相比，C 掺杂能更有效地进入 MgB_2 晶粒和晶界。

关键词：MgB_2；掺杂；相转化；烧结；两步反应

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