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Effects of ZrH_2 doping and sintering temperature on the critical current density of MgB_2 wires

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Abstract

ZrH_2-doped MgB_2 wires, with the composition of Mg:ZrH_2:B = $(1 - x)$:x:2 ($x = 0\%$, 5%, 8%, 10%, 12%, 15%), were fabricated through the in situ powder-in-tube method by using low carbon steel tubes as sheath materials. Samples were sintered at 700 °C, 750 °C, 800 °C and 900 °C for 2 h respectively in a flow of high purity argon. It is found that the amount of ZrB_2 increases with the doping ratio, and the content of Fe_2B increases with the sintering temperature. Critical current density (J_c) of all the doped samples decreases with the increase of sintering temperature, but the optimum doping ratio goes up correspondingly. Among all the doped samples, the samples of $x = 5\%$ and $x = 8\%$ exhibit better J_c properties at the sintering temperature of 700 °C, but the samples of $x = 10\%$, 12% and 15% present higher J_c values when sintered at 900 °C.

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1. Introduction

The discovery of superconductivity in MgB_2 with critical temperature of 39 K [1] has stimulated a lot of interests from scientists. Compared with

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high temperature superconductors, MgB_2 has no weak-link problem at grain boundaries [2], and the cost of raw materials is low. Therefore, MgB_2 is believed a promising candidate for the engineering applications in the temperature range of 20–30 K.

Many methods have been tried to fabricate MgB_2 wires [3–8], in which powder-in-tube (PIT) technique is an effective one. However, the critical current density (J_c) of MgB_2 usually decreases rapidly with the increase of magnetic field (B), due to the lack of pinning centers. Fortunately, it is reported that chemical doping can improve the J_c and flux pinning of MgB_2 superconductors effectively [9–13]. Ma et al. [13] demonstrated that the J_c of MgB_2/Fe tape had been improved by the 5 at% doping of $ZrSi_2$, ZrB_2 and WSi_2, respectively, but the doping ratios have not been optimized in their investigation. Feng et al. [11] confirmed that all the Zr-doped MgB_2 bulk samples have better performance than the undoped one, and the highest J_c of 2.1×10^6 A/cm^2 in 0.56 T at 5 K and 1.83×10^6 A/cm^2 in self-field at 20 K had been achieved in the $Mg_{0.9}Zr_{0.1}B_2$ sample.

In this paper, MgB_2 wires were fabricated by using ZrH_2 as dopant. As ZrH_2 decomposes to be Zr and H_2 at high temperature, we believe it can act as good as Zr powders for the improvement of MgB_2 performances. Therefore, we have paid our attentions to the optimum doping ratio of ZrH_2 and its relation with the sintering temperatures.

2. Experimental

ZrH_2-doped MgB_2 wires were fabricated by using the in situ PIT method. Mg (100–200 mesh, 99%), ZrH_2 (1250 mesh, 90%) and B (325 mesh, 99%) powders with the composition of $(1 - x)$:x:2 (doping ratio $x = 5\%$, 8%, 10%, 12%, 15%) were ground together in agate mortar for 3 h in air. Mixtures were properly filled into low carbon steel tubes (outer diameter: 16 mm, inner diameter: 12 mm). These composite tubes were groove-rolled, with four times of intermediate annealing performed at 400 °C, 450 °C, 590 °C and 580 °C for 1 or 2 h, respectively, to recover the plasticity and ductility of the low carbon steel. Subsequently, they were drawn to wires with the diameter of 1.6 mm. In the end, short samples were heated up to 700 °C, 750 °C, 800 °C, 900 °C and sintered for 2 h respectively in a flow of high purity argon. Then furnace-cooled to room temperature. Undoped MgB_2 wire ($x = 0$) was fabricated by using the same method, but only having two times of intermediate annealing at 590 °C and 580 °C, respectively.

Phase identification was performed by using the X-ray diffractometer. Microstructure analysis was carried out by scanning electron microscopy (SEM). Critical current (I_c) was measured by the standard four-probe resistance method in magnetic fields up to 7 T at 4.2 K. The criterion for the I_c definition was 1 μV/cm. J_c was obtained by dividing I_c by the cross-sectional area of the superconducting core.

3. Results and discussion

Fig. 1 illustrates X-ray diffraction (XRD) patterns of x mol ZrH_2-doped samples. MgB_2, ZrB_2, MgO, Fe_2B, δ-ZrH_2 and Mg can be identified in the samples sintered at 700 °C. The appearance of ZrB_2 is because that ZrH_2 decomposed and reacted with B during the sintering process, as shown following:

$$ZrH_2 \rightarrow Zr + H_2$$
$$Zr + 2B \rightarrow ZrB_2$$

As the relative peak intensity of ZrB_2 increases with the increasing of x, we believe the amount of ZrB_2 rises up correspondingly. However, the existence of δ-ZrH_2 indicates that ZrH_2 did not decompose thoroughly when sintered at 700 °C.

Fe_2B appears mainly as the interface layer between the sheath materials and the superconducting core. It is the formation of Fe_2B that consumed some B atoms and led to the surplus of Mg.

As the sintering temperature increasing, the phase compositions of these samples change slightly. No δ-ZrH_2 can be found in all samples sintered at 750 °C, such as shown in the sample $x = 8\%$. MgB_4 appears in the samples sintered above 850 °C, especially at 900 °C. The concentration of