Improved critical current densities in B$_4$C doped MgB$_2$ based wires

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Abstract

An improvement of the transport critical current density, $J_c$, of MgB$_2$ wires was obtained after the addition of 10 wt% B$_4$C powders, after reaction at 800°C: $J_c$ values of $1 \times 10^4$ A cm$^{-2}$ at 4.2 K and 9 T were obtained for wires of 1.11 mm diameter in a Fe matrix. The starting mixture of Mg and B was doped with submicrometric B$_4$C, the ratio being Mg:B:B$_4$C = 1:2:0.08, corresponding to 10 wt% B$_4$C. For $T > 800°C$, a decrease of $J_c$ was found, due to the reaction with the Fe sheath. In order to investigate the origin of the improvement of the transport properties for heat treatments up to 800°C, x-ray diffraction measurements were performed. A decrease of the lattice constant $a$ from 3.0854 to 3.0797 Å was found, thus suggesting an effect of the substitution of carbon on the properties of the wires. A comparison with the literature data shows that the addition of B$_4$C powders leads to the second highest improvement of $J_c$ reported so far after SiC, thus constituting an alternative for future applications.

1. Introduction

The high critical temperature of MgB$_2$ [1] with respect to the industrial low temperature Nb$_3$Sn and NbTi renders this compound suitable for applications at 20 K. Many groups are currently developing wires and tapes conductors by powder-in-tube procedures, either by the ex situ [2–4] or by the in situ technique [5, 6]. The $J_c$ values of properties of in situ wires experienced a strong improvement after introducing SiC nanopowders [7], the effect being attributed to the substitution of carbon for boron. The effect of adding B$_4$C powders has been studied by various authors [8–11], who found that B can be partially replaced by C in the MgB$_2$ phase. This was concluded by Yamamoto et al and by Balaselvi et al [8, 9] from the change of the lattice parameter $a$ of MgB$_2$, while Ribeiro et al [10] reported a decrease of $T_c$. Another author reported higher values of $B_{c2}$ for MgB$_2$ bulk samples after B$_4$C additions [12]. Since all these works have been performed on bulk samples, we have investigated the possibility of fabricating in situ wires by using B$_4$C submicron powder additions, in order to exploit the potentialities of this compound. We report in the present paper a sizable increase of $J_c$ after B$_4$C doping of in situ MgB$_2$/Fe wires. The enhancement of $J_c$ is still lower than for SiC additions, but B$_4$C additions could possibly constitute an alternative in view of an enhancement of the transport properties of MgB$_2$.

2. Experimental details

Monofilamentary wires were prepared by the powder-in-tube technique using Mg (99.8% pure, ~325 mesh) and amorphous B (oxygen content: 1.02%, micrometric particle size) at the stoichiometric ratio, adding 10 wt% of B$_4$C submicron powders (average particle size: 500 nm). The ratio between the starting compounds was chosen to be Mg:B:B$_4$C = 1:2:0.08, corresponding to 10 wt% B$_4$C. The precursors were mixed and then inserted in 10 cm long Fe tubes (99.5% pure) of diameter out and diameter in of 8 and 5 mm, respectively. The diameter of the tubes was successively reduced applying a combination of swaging and drawing, and wires of 1.11 and 0.657 mm diameter were obtained. The wires were heat treated under Ar flow at various temperatures from 670 to 900°C and for various
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3. Results

The XRD patterns of the powder extracted from some of the doped conductors are shown in figure 2. At 670 °C, the MgB₂ superconducting phase has already been formed, as for undoped wires, and is coexisting with boron carbide and some MgO. At 670 and 720 °C, some free Mg and traces of the two other phases MgB₂C₂ and Mg₂C₃ are also present, indicating that the reaction is not yet complete.

With higher reaction temperatures, the intensities of the peaks corresponding to B₄C and Mg are progressively reduced, leaving only the reflections due to MgB₂ and MgO. Some Fe peaks, present in all patterns, are due to residual Fe after extracting the powder from the matrix. These data are compatible with other works [8–11] which revealed the same secondary phases in the superconducting powder. It has to be noted that the presence of the Fe sheath and the excess of B in the starting mixture have an influence on the kinetics of the reaction [13]. A cross section of the wire after 1 h at 800 °C obtained using an optical microscope (figure 3) shows a reaction layer of ~8 μm thickness [13–15], confirming a partial interaction of the superconducting filament with the sheath. Table 1 shows the variation of the lattice parameters a and c as a function of the reaction temperature and the critical temperature measured via susceptibility. This variation shown in figure 4 for the parameter a suggests that the reaction between B₄C with the two main elements leads to a substitution of the boron by carbon in the ab planes [8–12, 16, 17]. Comparing the lattice parameters with those of C doped bulk samples [8, 17], it is concluded that the amount of C substituting for the B atoms is lower than the nominal one, Mg:B:B₄C = 1:2:0.08, but that the substituted C content increases with reaction temperature.

Measurements of the critical current density Jₑ versus B were performed at 4.2 K for various reaction conditions. For each set of temperature and reaction time, several wires were measured, in order to verify the homogeneity inside the wires. The results are shown in figure 5 where the critical current densities Jₑ of the pure and the B₄C doped wires of 1.11 mm diameter are compared. As expected, the critical current densities of the undoped wire become progressively smaller with higher reaction temperatures. This is in contrast
Figure 4. Lattice parameter $a$ versus reaction temperature showing a shrinking of the $ab$ plane due to the interaction of the dopant B$_4$C with the basic elements Mg and B.

Figure 5. Critical current density $J_c$ versus applied magnetic field $B$ for the pure and the B$_4$C doped conductors after annealings at various temperatures.

Figure 6. Critical current density $J_c$ versus applied magnetic field $B$ for the B$_4$C doped wire after reaction at 800 and 900°C.

Figure 7. Critical current density $J_c$ versus applied magnetic field $B$ at 4.2 and 20 K for B$_4$C doped wire of 1.11 and 0.657 mm diameter, reacted for 1 h at 800°C.

Figure 8. Comparison between the critical current density $J_c$ and the applied magnetic field $B$ for various added MgB$_2$ wires and tapes with B$_4$C and SiC addition.

to the case for B$_4$C doped wires, where an enhancement of $J_c$ with the reaction temperature is observed, in agreement with the results on bulk samples [8]. The highest value measured so far for a wire with 10 wt% B$_4$C is $1 \times 10^4$ A cm$^{-2}$ at 9 T. The effect of a further enhancement of the reaction temperature on $J_c$ for a B$_4$C doped wire is shown in figure 6. After longer reaction times at 800°C, only a small reduction of the critical current density $J_c$ is observed, in contrast to a considerably larger reduction at 900°C.

In order to confirm these results, additional wires doped with 10 wt% B$_4$C submicron powder particles were fabricated, again with diameters of 1.11 and 0.657 mm. Measurements of the critical current density versus $B$ were performed both at 4.2 and at 20 K and are shown in figure 7. The results confirm the data for the first series of wires, with a $J_c$ value of $10^4$ A cm$^{-2}$ at 4.2 K and 9 T. The same $J_c$ value was obtained at 20 K and 4 T.

4. Discussion

The present fabricated wires show an improvement of the transport $J_c$ of MgB$_2$ wires when adding 10 wt% B$_4$C submicron powders, at reaction temperatures as low as 800°C. A comparison with other $J_c$ values is shown in figure 8, showing a sizable increase of $J_c$ when comparing to the B$_4$C doped bulk samples obtained by Yamamoto [8]. These
authors [8] started with a different nominal composition, and the reaction occurred at a different temperature. As suggested by Yamamoto [8] and by Ribeiro et al [10], the addition of B4C leads at the same reaction temperature to a higher solubility of pure carbon than the addition of carbon, which allows performing the reaction at lower temperatures: in the present work, a change in the lattice parameter is already observed at 720 °C. This is the main reason for the enhanced \( J_c \) values in the present work: the other authors added B4C to MgB2 bulk samples using considerably higher temperatures [9, 10, 17].

In our case, a deterioration of the transport properties of the conductors was observed at 900 °C, which is attributed to reaction with the Fe matrix [13–15]. It is important to note that the powders used were mixed with an excess of B with respect to the stoichiometric ratio, thus probably compensating for the B losses due to the interaction with the sheath (at least up to 800 °C). This fact is confirmed by the measurements on the B4C doped wire with 0.657 mm diameter (figure 7). In this case, the critical current density \( J_c \) was lower than that of the same conductor deformed to 1.11 mm, reacted at the same temperature (800 °C). The influence of the reaction layer on the smaller wires is expected to be more effective.

It is known that MgB2 wires with SiC nanopowder additions reach higher values of \( J_c \), the highest being \( 10^4 \) A cm\(^{-2}\) at 12 T [18–20]. However it has to be noted that our B4C powders have considerably larger size (500 nm). In addition, no effort was undertaken to further densify the powder mixture in the filaments. The results obtained are promising for further enhancement of the transport properties of the B4C added wires. It is expected that further improvements could be obtained by using a harder matrix, e.g. stainless steel, by reducing the size of the filaments and by the optimization of the annealing conditions.

5. Conclusions

In this study, we have investigated the transport properties of \( \text{in situ} \) B4C doped MgB2 conductors. Measurements of transport properties revealed a marked enhancement of the current carrying capability of the wires after reaction at 800 °C. The analysis of the reacted powder extracted by the wires revealed a shrinkage of the lattice parameter \( a \), thus indicating a substitution of B by C. The present results confirm the potential role of B4C, besides SiC, as an alternative addition for improving the transport properties of MgB2 based conductors.

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