Comparative study of different chemical doping effect on the $J_c$-$B$ properties of MgB$_2$ tapes

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Abstract. The effect of chemical doping on the critical current density of MgB$_2$ tapes is studied. As impurities, we tried silicides, carbon and organic compound. Most of them lead to an obviously improvement of critical current density ($J_c$), and weaken its field dependence. For the silicides addition, the reaction products, such as Mg$_2$Si play an important role in the enhancement of flux pinning ability. For the doping of carbon containing impurities, carbon substitution to boron contributes significantly to the enhancement of flux pinning ability and upper critical field, and eventually improves the $J_c$-$B$ performance of MgB$_2$ tapes. By modifying starting materials preparation process and optimizing carbon source, further improvement of in-field $J_c$ is expected.

1. Introduction

The discovery of superconductivity in MgB$_2$ initiated enormous scientific interests not only in basic physics but also in practical applications. The much higher transition temperature ($T_c$) [1], low material cost, chemical simplicity and weak-links-free of MgB$_2$ caused researchers to assume that MgB$_2$ could be used at temperatures around 20 K as the conductor of a cryogen-free magnet. One of the most important applications of superconductors is in the area of high current and high field, where high $J_c$ in magnetic fields is essential [2]. However, $J_c$ of MgB$_2$ drops rapidly with increasing magnetic field due to the low upper critical field ($H_{c2}$) and poor flux pinning ability. Various methods have been tried to improve the flux pinning and $H_{c2}$ of MgB$_2$, such as high-energy ball milling [3], irradiation [4], hot isostatic [5], magnetic field processing [6] and chemical doping [7-9]. As a simple and practical method, chemical doping seems to be the best route to improve the $J_c$-$B$ property of MgB$_2$, as reported so far [10-14]. There are basically two kinds of chemical doping effects: addition effects or substitution effects. The primary difference between addition and substitution effects is that the particles doped by addition will remain between the grains only, while some elements are substituted into MgB$_2$ lattice for the particles doped by substitution. The particles existed at grain boundaries will producing a substantial effect on the grain connectivity and grain growth, whereas the dopant substituted into MgB$_2$ lattice will provide impurity scattering and yield changes of electronic state, lattice distortions, etc.

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Of all impurity additions that had been undertaken, silicides and various carbon sources have been hotly studied. In this paper, we will review the process of experimental efforts in the doping of MgB$_2$, especially for WSi$_2$, ZrSi$_2$, MoSi$_2$, SiC, Si/N/C, C, and organic compound doping.

2. Silicides doping

The doping effect of silicides, including WSi$_2$, Mg$_2$Si, SiO$_2$ [11], MoSi$_2$ [15], ZrSi$_2$ [16], SiC [10], Si/N/C [7], have been investigated on $J_c$ performance in MgB$_2$. It is found that $J_c$ enhancement was obtained for all of these silicides except for SiO$_2$, but the improvement caused by different silicides doping varies from one to another. Figure 1 shows a comparison of the $J_c$ values of some silicides doped MgB$_2$ samples by the authors’ group [7, 15, 16]. For MoSi$_2$ doped samples, MoSi$_2$ phase is clearly seen as one of main impurities from XRD patterns, and there is no reaction produced material such as Mg$_2$Si appeared [15]. This means that MgB$_2$ is inert with respect to MoSi$_2$. The similar result was also found for WSi$_2$-doped tapes, as reported by Ma et al. [17]. On the contrary, the addition of ZrSi$_2$ in MgB$_2$ tapes resulted in the formation of Zr$_3$Si$_2$ and Mg$_2$Si, no diffraction peaks of ZrSi$_2$ phase was observed, suggesting that there were reaction between MgB$_2$ and ZrSi$_2$ [16]. The reaction induced fine particles play an important role in the enhancement of flux pinning ability. This may partially explain the different $J_c$-B properties in MoSi$_2$ and ZrSi$_2$ doped samples.

![Figure 1. $J_c$-B properties of various silicides doped MgB$_2$ tapes.](image)

In comparison with other silicides doped MgB$_2$ samples, the enhancement of $J_c$-B properties were much significant in SiC doped ones, as can be seen clearly from figure 1. According to Dou’s study [18], SiC can react with Mg at low temperature to form Mg$_2$Si, and release C at the same time. Thus highly dispersed fine particles, such as Mg$_2$Si and C can be embedded into MgB$_2$ matrix, improving the flux pinning ability of MgB$_2$. It is known that in SiC doped samples, high $J_c$-B properties are often obtained when the samples were sintered at relatively low temperatures (600-650°C) [2]. A lower sintering temperature means smaller MgB$_2$ grain size and a larger amount of grain boundary in MgB$_2$ core. As reported by Kiuchi et al. [19], grain boundary scattering will improve the $H_{c2}$ of MgB$_2$. So we think that high $H_{c2}$ values found in SiC doped samples is the conjunct result of the C substitution and the larger amount of grain boundaries. The Si/N/C doped tapes exhibited lower $J_c$ value compared to SiC doped ones. This may be due to the lower chemical reactivity of Si or/and C element in Si/N/C than that in SiC [7].
3. Carbon doping

The effect of carbon doping on the $J_c$-$B$ properties of MgB$_2$ using amorphous carbon [9, 20], graphite [21, 22], carbon nanotubes [23], diamond [24] and carbon nanohorns [25] have been investigated by several groups. In fact, all the carbon substitutions resulted in much higher $J_c$ values in MgB$_2$ than those for the pure material. The authors’ group studied the nano-C doping effect on the critical temperature, lattice parameter, $J_c$-$B$ property, $H_{c2}$ and flux pinning of MgB$_2$ tapes [9, 26-28]. It is found that the superconducting properties of C doped samples are influenced by C doping level, sintering temperature, precursor material process, etc. Figure 2 shows the sintering temperature and ball milling effect on $J_c$-$B$ properties of nano-C doped MgB$_2$ tapes. From figure 2 we can see that the $J_c$ values of C doped tapes were improved when sintering temperature increased from 700°C to 900°C. As we have discussed earlier, high temperature sintering will increase the MgB$_2$ grain size, and decrease the number of grain boundaries. This will have a negative effect on $J_c$-$B$ property of MgB$_2$ tapes. So the $J_c$ value enhancement for samples sintered at higher temperature is mainly related to more C substitution in MgB$_2$ lattice. On the other hand, $J_c$ values were significantly improved when the mixture was homogenized by ball milling. Moreover, it should be noted that the $J_c$ value of ball-milled C doped sample sintered at 700°C were nearly the same to that of hand-milled one sintered at 900°C. This suggests that the sintering temperature can be lowered by ball-milling in C doped samples.

As mentioned in earlier paragraphs, the substitution of C for B is believed to be the main reason for $J_c$-$B$ property improvement in C doped MgB$_2$ tapes. For MgB$_2$, the high-temperature superconductivity originates from the strong electron-phonon coupling in $\sigma$ bands. So the substitution of B by C would introduce a net of intragranular defects due to crystal lattice distortions and local fluctuations of the superconducting order parameter. Both of them can strongly improve the flux pinning properties of MgB$_2$ [29]. At the same time, the carbon substitution has a great impact on the carrier density and impurity scattering [30], which will enhance the $H_{c2}$, $H_{irr}$ of MgB$_2$. Eventually, the $J_c$-$B$ properties of C doped MgB$_2$ tapes are significantly improved.

Figure 3 shows the exponential $n$ factor of C doped MgB$_2$ tapes. The $n$ factors were obtained by fitting the relation $E=E_c(l/l_c)^n$ to our $E$-$I$ curves in the electric field range of $0.1 \mu$ V/cm<$E$<$1 $\mu$ V/cm. It can be seen that the $n$ factors decrease almost linearly with increasing magnetic fields, although the data are scattering because of the difficulty in the determination of $n$ factors. The same phenomenon was found in SiC doped samples [31]. The high $n$ factors of C doped samples are very beneficial for practical uses of MgB$_2$ wires and tapes. For the 10% C doped samples sintered at 900°C, the $n$ factors were lower than those of other samples.

Figure 2. $J_c$-$B$ properties of nano-C doped MgB$_2$ tapes.

Figure 3. Field dependence of the exponential $n$ factors in C doped MgB$_2$ tapes.
4. Organic compound doping

Inspired by the C doping, Yamada et al. [32] using aromatic hydrocarbons as C source, Kim et al. [33] using malic acid as C source approached C doping in MgB$_2$. It is claimed that the doped carbohydrate will decompose at temperatures below the formation temperature of MgB$_2$, hence producing highly reactive and fresh C on the atomic scale, which is beneficial for the substitution of C to B. We have investigated the effect of stearic acid, stearate, and maleic anhydride doping on the microstructure and superconducting properties of Fe-sheathed MgB$_2$ tapes [34, 35]. Our results demonstrated that both the $J_c$ and flux pinning ability of MgB$_2$ tapes are significantly improved through stearic acid, stearate and maleic anhydride doping. Figure 3 shows the $J_c$-$B$ properties of MgB$_2$ tapes using C$_{18}$H$_{36}$O$_2$, C$_{36}$H$_{70}$MgO$_4$, C$_{36}$H$_{70}$ZnO$_4$, C$_4$H$_2$O$_3$ as dopant. Although they are all very effective in the enhancement of $J_c$-$B$ properties of MgB$_2$ tapes, there are some differences. Better high field performance was found in stearic acid doped samples than in stearate doped ones. This may be due to the higher net C percentage in stearic acid than that of other two stearate dopant [34]. On the other hand, although the $J_c$ values of C$_4$H$_2$O$_3$ doped samples were a little lower than those of C$_{18}$H$_{36}$O$_2$ doped ones at 9 T, they exceed in higher fields. The different O element containing in these dopant may be responsible for this. Using C$_4$H$_2$O$_3$ as dopant, many MgO fine particles were produced in MgB$_2$ matrix. According to Kovac’s work, MgO particles existed at grain boundaries will worsen the inter-grain connectivity, but improve the flux pinning ability at the same time [36].

![Figure 4. $J_c$-$B$ properties of organic compound doped MgB$_2$ tapes.](image)

5. Conclusion

In summary, the $J_c$-$B$ properties of MgB$_2$ can be significantly improved by chemical doping, and C containing material is the most favorable dopant. $H_{c2}$ and flux pinning ability are enhanced when C were substituted into MgB$_2$ lattice. The reaction induced fine impurity particles, such as Mg$_2$Si, Mg$_2$C$_3$ can serve as the effective pinning centers. The O element in organic compound has some effect on the MgO formation when they are used as doping material. High energy ball milling has been proved to be a potential method in the enhancement of $J_c$-$B$ property of MgB$_2$. We believe that further improvement in $J_c$-$B$ is expected by either optimizing the C source material or modifying the starting materials and MgB$_2$ sample preparation process.
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