Carbohydrate doping to enhance electromagnetic properties of MgB2 superconductors

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2006

Publication Details

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Abstract
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Keywords
Carbohydrate, doping, enhance, electromagnetic, properties, MgB2, superconductors

Disciplines
Engineering | Physical Sciences and Mathematics

Publication Details

This journal article is available at Research Online: http://ro.uow.edu.au/aiimpapers/232
Carbohydrate doping to enhance electromagnetic properties of MgB_2 superconductors

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(Received 21 July 2006; accepted 23 August 2006; published online 3 October 2006)

The effect of carbohydrate doping on lattice parameters, microstructure, T_c, J_{c, irr}, and H_{c2} of MgB_2 has been studied. In this work the authors used malic acid as an example of carbohydrates as an additive to MgB_2. The advantages of carbohydrate doping include homogeneous mixing of precursor powders, avoidance of expansive nanoadditives, production of highly reactive C, and significant enhancement in J_c, H_{c, irr}, and H_{c2} of MgB_2, compared to undoped samples. The J_c for MgB_2 + 30 wt % C_4H_6O_5 sample was increased by a factor of 21 at 5 K and 8 T without degradation of self-field J_c.

With the relatively high critical temperature (T_c) of 39 K (Ref. 1) and the high critical current density (J_c) of >10^5 cm^2 V^{-1} s^{-1} in moderate fields, magnesium diboride (MgB_2) superconductors could offer the promise of important large-scale applications to be operated at 20 K. A significant enhancement in the electromagnetic properties of MgB_2 has been achieved through doping with various forms of carbon (C). To take advantage of its both the upper critical field (H_{c2}) and J_c are essential. Attempts to accomplish this have invoked the introduction of numerous techniques including chemical doping, irradiation, and various thermomechanical processing techniques. Chemical doping is a simple and readily scalable technique. Since MgB_2 has a relatively large coherence length and small anisotropy, the fluxoids to be pinned are stringlike and amenable to pinning by inclusions and precipitates in the grains.

Among the numerous forms of C-containing dopants, SiC doping has achieved a record high in-field J_c(B), H_{c2}, and irreversibility (H_{c, irr}) in MgB_2. These record high properties have been confirmed and reproduced by many groups, and the performance records remain unbroken up to now. However, the best high-field J_c values achieved in the SiC doped MgB_2 wires were compromised by the reduction in self-field and low-field J_c. Although nanosize precursors were chosen for the doping process it is a great challenge to achieve homogeneous distribution of a small amount of nanodopants within the matrix materials through solid state mixing. There are always agglomerates of nanoadditives in the precursors. For various forms of C doping, the substitution of C for boron (B) cannot be achieved at the same temperatures as that of the MgB_2 formation reaction due to their poor reactivity.

In order to overcome these problems we proposed to use a carbohydrate such as DL-malic acid (C_4H_6O_5) as the dopant. The significant advantages of carbohydrate are as follows. (1) Carbohydrates can be dissolved in a solvent so that the solution can form a slurry with B powder. After evaporating the solvent the carbohydrate forms a coating on the B powder surfaces, giving a highly uniform mixture. (2) The carbohydrates in the mixture melt at lower temperatures and decompose at temperatures below the formation temperature of MgB_2, hence producing highly reactive and fresh C on the atomic scale, as well as a reducing reagent, carbon monoxide, which may convert boron oxide to B, reducing the impurities in B powder. (3) Because of the high reactivity of the freshly formed C, the C substitution for B can take place at the same temperature as the formation temperature of MgB_2. The simultaneous dual reactions promote C substitution for B in the lattice and the inclusion of excess C within the grains, resulting in the enhancement of J_c, H_{c, irr}, and H_{c2}.

In this study, therefore, we used malic acid as a representative of carbohydrate dopant. We fabricated MgB_2 + C_4H_6O_5 samples with different addition levels. The lattice parameters T_c, J_{c, irr}, H_{c2}, and microstructures are presented in comparison with the undoped reference MgB_2. MgB_2 pellets were prepared by an in situ reaction process with the addition of C_4H_6O_5. The selected amount of C_4H_6O_5 (99%), from 0 to 30 wt % of total MgB_2 was mixed with an appropriate amount of B (99%) powder in toluene (C_8H_18, 99.5%). This slurry was dried in vacuum so that the B powder particles were coated by the C coming from C_4H_6O_5. Since the decomposition temperature of C_4H_6O_5 was at around 150 °C, this uniform composite was then mixed with an appropriate amount of Mg (99%) powder. These mixed powders were ground, pressed, and then sintered at 900 °C for 30 min under argon gas. All samples were characterized by x-ray diffraction (XRD), field emission gun-scanning electron microscopy (FEG-SEM), J_c, T_c, H_{c, irr}, and H_{c2}. The lattice parameters were obtained from Rietveld refinement.

Table I shows the measured data for the undoped MgB_2 and MgB_2 + C_4H_6O_5 samples with different addition levels. The lattice parameters calculated from XRD show a large decrease in the a-axis parameter with 10 wt % C_4H_6O_5 and a small further drop in a with increasing C_4H_6O_5 addition level, but no change in the c-axis parameter. This is an indication of the C substitution for B. The actual C substitution level can be estimated from the a-axis change. It should be noted that the net C percentage addition is only 36% of the C_4H_6O_5 addition. The actual C substitution levels of 1.9–2.3 at % of B at three doping levels are clearly higher than those with other forms of C dopants, which is attributable to the high reactivity of fresh C released from the...
composition of C₄H₆O₅ at low temperature. The increase in sintering temperature improves both the crystallinity and the C substitution for B. The former will increase $T_c$, while the latter will decrease $T_c$. As a compromise, these two opposing factors result in a high level of C substitution for B with a relatively small drop in $T_c$. The high-field $J_c$'s of the MgB₂ +C₄H₆O₅ samples were much higher than that of the undoped MgB₂. Specifically, it should be noted that the self-field $J_c$ of MgB₂+C₄H₆O₅ samples was not reduced at addition levels as high as 30 wt % C₄H₆O₅; hence the connectivity between MgB₂ grains was not affected by addition with C₄H₆O₅. Although there is a possibility of the formation of H₂O during sintering due to the decomposition of C₄H₆O₅, there was no degradation in self-field $J_c$, even for 30 wt % C₄H₆O₅ added to MgB₂. This may be attributable to the fact that the decomposition products, C and CO, of C₄H₆O₅ reduced B₂O₃ and hence increased the effective cross section of the superconductor.

Figure 1(a) shows the magnetic field dependence of $J_c$ in all samples at 20 and 5 K. It should be noted that $J_c$ values in high field were increased by more than an order of magnitude. For example, the $J_c$ value of 2.5 × 10⁴ A cm⁻² at 5 K and 8 T for MgB₂+30 wt % C₄H₆O₅ sample is higher than that of the undoped MgB₂ by a factor of 21. In addition, there was no $J_c$ degradation in self-field for the MgB₂ +30 wt % C₄H₆O₅ sample. These findings can be further supported by the flux pinning results. Figure 1(b) plots the field dependence of the volume pinning force, $F_p=J_c B$, of all samples at 20 K. The $F_p$ is normalized by the maximum volume pinning force $F_{p,\text{max}}$. The flux pinning for the MgB₂+C₄H₆O₅ samples was significantly higher than that of the undoped one at $B>1.5$ T. This result indicates that the $F_p(B)$ of MgB₂+C₄H₆O₅ samples was improved by the C substitution effect and nano-C inclusions within the grains.

The normalized temperature dependence of $H_{irr}$ and $H_{c2}$ for all samples is shown in Fig. 2. Significantly enhanced $H_{irr}$ and $H_{c2}$ for MgB₂+C₄H₆O₅ samples were observed, suggesting that C substitution into B sites results in an enhancement in $H_{irr}$ and $H_{c2}$. The steeper slopes of $H_{irr}$ for MgB₂+C₄H₆O₅ samples exceeded $H_{c2}$ of undoped MgB₂ below a

![FIG. 1. Superconducting properties of undoped MgB₂ and MgB₂+C₄H₆O₅ samples with different addition levels: (a) Magnetic field dependence of $J_c$ in all samples at 20 and 5 K; (b) field dependence of the volume pinning force, $F_p=J_c B$, of all samples at 20 K. The $F_p$ is normalized by the maximum volume pinning force $F_{p,\text{max}}$.](image)

![FIG. 2. Normalized temperature dependence of $H_{irr}$ and $H_{c2}$ for undoped and C₄H₆O₅ doped samples. $H_{irr}$ and $H_{c2}$ were defined as $H_{irr}=0.9R(Tc)$ and $H_{c2}=1.1R(Tc)$ from the R vs T curve.](image)
temperature of 22 K. The resistivities $\rho$ for the undoped and MgB$_2$+C$_4$H$_6$O$_5$ samples are 34 and 80–90 $\mu\Omega$ cm at 40 K, respectively, as shown in Table I. The increased resistivity for MgB$_2$+C$_4$H$_6$O$_5$ samples indicates the increased impurity scattering as a result of C substitution into B sites. However, this effect may be offset by the increase in C sub-act as a sintering aid to improve the crystallinity. The grain improvement in grain connectivity. This is well evidenced by the fact that the self-field $J_c$, $H_{\text{irr}}$, and $H_{c2}$ performances at all the operating temperatures and over the entire field range. This finding opens a direction for the manufacture of nanodoped materials using the carbohydrate solution route, which solves the agglomeration problem, avoids the use of expensive nanoadditives, and achieves improved performance properties.

In summary, carbohydrate doping results in a small depression in $T_c$ but significantly increases the C substitution level, reduces the impurities, and hence improves $J_c$, $H_{\text{irr}}$, and $H_{c2}$ performances at all the operating temperatures and over the entire field range. This finding opens a direction for the manufacture of nanodoped materials using the carbohydrate solution route, which solves the agglomeration problem, avoids the use of expensive nanoadditives, and achieves improved performance properties.

The authors gratefully acknowledge helpful discussion with E. W. Collings and M. Tomsic, and financial support from the Australian Research Council, Hyper Tech Research Inc., and CMS Alphatech International Ltd.