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Improvement of $J_c$ and $H_c2$ in MgB$_2$ superconductor with citric acid addition

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Abstract This paper reports on the fabrication and characterization of citric acid (CA)-C$_6$H$_8$O$_7$ added MgB$_2$ superconductor. The relationships between microstructures, critical current density ($J_c$), critical temperature ($T_c$), upper critical field ($H_{c2}$), irreversibility field ($H_{irr}$), and normal state resistivity for 10 wt% C$_6$H$_8$O$_7$ added MgB$_2$ samples sintered at temperatures from 650°C to 950°C were systematically studied. A reduction in $T_c$ and in lattice parameter $a$ due to the C substitution and possible oxygen (O) effects occurs with C$_6$H$_8$O$_7$ addition. $J_c$, $H_{c2}$, and $H_{irr}$ are significantly enhanced, however, with the addition of C$_6$H$_8$O$_7$. All the samples exhibit $J_c$ above $10^4$ A/cm$^2$ at 5 K and 8 T. This value is higher than for the un-doped MgB$_2$ by a factor of 9. The significant improvement in the superconducting properties is attributed to the lattice distortion due to the C and possible oxygen (O) substitution for boron, with the C and O coming from the decomposition of C$_6$H$_8$O$_7$.

1. Introduction

MgB$_2$ superconductor is a promising candidate for large-scale applications at around 20 K due to its high critical temperature ($T_c$) ~ 39 K [1], as well as its cheap raw materials and simple manufacturing processing. It has been reported that a significant improvement in the critical current density ($J_c$) in MgB$_2$ can be achieved through chemical doping with nano-SiC, nano-C, carbon nanotubes (CNT), etc. [2-5], because these nanomaterials can reduce the reaction energy and decrease the reaction temperature. The C can enter the MgB$_2$ lattice by occupying boron (B) sites, and thus $J_c$ and $H_{c2}$ are significantly enhanced due to the increased impurity scattering in the two-band MgB$_2$. However, such nanomaterial doping processes in MgB$_2$ superconductor are limited by the difficulty in dispersing nanosized particles and by the poor reactivity between B and C, which will lead to inhomogeneity and increase the proportion of impurity phases, thus degrading the superconducting properties. Mickelson et al. first discovered B$_4$C as a C source [6], and Ribeiro et al. [5] also reported that B$_4$C has high potential as a C source, because during the decomposition of B$_4$C, highly active C particles are formed. However, they showed that a higher sintering temperature and longer sintering time are required. Dou et al. [7] reported enhanced superconducting properties of C doped MgB$_2$ from using SiC as a C source, with only a low temperature (~ 650 °C) sintering procedure required. Moreover, Dou’s group has indicated that carbohydrates (CH) are good candidates to be C source materials for C doping into MgB$_2$ [8]. They decompose at temperatures that are below the formation temperature of the MgB$_2$ phase itself, and hence can produce highly reactive C on the atomic scale.

In this study, we report on the fabrication and superconducting properties of C doped MgB$_2$ superconductor when citric acid (C$_6$H$_8$O$_7$) is used as the C source. The amount of C$_6$H$_8$O$_7$ additive was...
kept constant at 10 wt%, and the effects of sintering temperature on the microstructure and the superconducting properties of $\text{C}_6\text{H}_8\text{O}_7$ doped $\text{MgB}_2$ were studied.

2. Experimental procedure

$\text{MgB}_2$ bulks with addition of $\text{C}_6\text{H}_8\text{O}_7$ were prepared by an in situ reaction process. 10wt% $\text{C}_6\text{H}_8\text{O}_7$ (Aldrich, 99%) of total $\text{MgB}_2$ was mixed with an appropriate amount of B (99%) in toluene (99.5%). This slurry was dried in a vacuum so that the B powder was encapsulated by or mixed with the C coming from $\text{C}_6\text{H}_8\text{O}_7$. This uniform composite was then mixed with an appropriate amount of Mg (99%) powder. These mixed powders were ground, pressed, and then sintered at 650°C to 950°C for 30 min under high purity argon (Ar) gas. The heating rate was 5°C min\(^{-1}\) under Ar. All samples were characterized by X-ray diffraction (XRD) and analyzed using Rietveld refinement XRD to determine the $a$ and $c$ lattice parameters and the MgO content. $T_c$ was defined as the onset temperature at which diamagnetic properties were observed. The magnetization of samples was measured at 5 and 20 K using a Quantum Design Physical Properties Measurement System (PPMS) with a magnetic field sweep rate of 50 Oe/s and amplitude up to 9 T. The magnetic $J_c$ was calculated from the height of the magnetization loop $M$ using the critical state model: $J_c = 12M_b/d(3b-d)$, with $b$ and $d$ the dimensions of the sample perpendicular to the direction of applied magnetic field and $d < b$. The magnetoresistivity $\rho(H,T)$ was measured with $H$ applied perpendicular to the current direction using the four probe method in the temperature range from 4.2 K to 300 K and the field range from 0 T to 9 T. The irreversibility field, $H_{irr}$, and $H_{c2}$ can be deduced using the criteria of 0.1 and 0.9 of $\rho(H,T)$, respectively.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of the doped samples sintered at 650°C to 950°C, as well as the un-doped sample sintered at 650°C. Analysis of the XRD patterns of the samples revealed that they are of $\text{MgB}_2$ phase with small amounts of MgO impurity.

![Fig. 1. X-ray diffraction patterns for the un-doped and 10 wt% citric acid added $\text{MgB}_2$ samples sintered at temperatures from 650°C to 950°C.](image)

Fig. 2 shows the $a$- and $c$-axis lattice parameters and the MgO content versus sintering temperature for the 10% $\text{C}_6\text{H}_8\text{O}_7$ added $\text{MgB}_2$ samples. It was found that both the $a$-axis and the $c$-axis lattice parameters calculated from XRD remain constant with increasing sintering temperature. From the $a$-axis data, we estimated that the amount of C substitution $x$ was about 0.03 in the Mg ($\text{B}_{1-x}\text{C}_x$)\(_2\) system,
according Li’s [9] calculations for all 10% C₆H₈O₇ added MgB₂ samples sintered at different temperatures. It is particularly interesting to note that the MgO content decreases with increasing sintering temperatures. This feature is contrary to the characteristics of normal MgB₂ samples, where the MgO percentages show a slight increase with increasing sintering temperature, since high temperature sintering increases MgO precipitates [10]. This indicated that there was more formation of carbon monoxide (CO), which is a product of the decomposition of the citric acid, at high sintering temperature and that this CO acted as a reducing agent to prevent the formation of oxides of Mg and B.

The full width at half maximum (FWHM) values as function of sintering temperature for all the samples studied are shown in Fig. 3. The in-plane FWHMs of the (110) and (100) peaks for the doped samples are larger than those of the corresponding peaks for the un-doped one. As the sintering temperature increased, the in-plane FWHM values slightly decreased. Because the (110) and (100) peaks reflect the lattice constant of the honeycomb B sheet, the broadening of this peak may suggest the occurrence of some distortion of the sheet and/or some grain size refinement. This result is consistent with the report of Yamamoto et al. [12], who observed that $H_{irr}$ increased with increasing FWHM of the (110) peak. A distortion of the honeycomb B sheet may result in an improvement in the intraband scattering, and thus enhance $H_{c2}$ through a reduction in the coherence length $\xi$. A decrease in the grain size could also result in peak broadening. Typical SEM images of samples sintered at various temperatures are shown in Figure 4. It can be seen that the grain sizes of all the CA added samples are smaller than in the un-doped sample, and the grain size of the CA added sample sintered at 850 °C is slightly larger than those of the other CA added samples.

Figure 5 shows the $T_c$ of all of the samples sintered at 650 to 950 °C for 30 min. The $T_c$ decreased with citric acid addition, when compared to the un-doped sample, but the $T_c$ shows slight variations with increasing sintering temperature. This could be caused by the inhomogeneity of the samples, or possibly by variations in the level of residual oxygen solubilised in the MgB₂, or in the amount of Mg evaporation, or by grain size and crystallinity variations in the samples sintered at different temperatures.

Fig. 6 shows the dependence of the $J_c$ on the applied magnetic field ($B$) at 5 and 20 K. The $J_c$ values for all of the doped samples reached $10^4$ A cm⁻² at 5 K and 8 T. These values are a factor of 6 higher than that of the un-doped MgB₂. We observed a crossover in the $J_c$ curves at 5 K when the applied magnetic field was around 6.5 T. The crossover might be considered as an indication of the increased grain boundary pinning strength in the samples with smaller grain size and possibly of different levels of dissolved oxygen in MgB₂ samples sintered at different temperatures. For example, the lower field $J_c$ of the 850 °C sintered sample was higher, and the high field $J_c$ was lower than that of the others.
Fig. 4. SEM images for the un-doped and 10 wt% citric acid added MgB$_2$ samples processed at temperatures from 650$^\circ$C to 950$^\circ$C.

Fig. 7 shows the temperature ($T$) dependence of $H_{\text{irr}}$ and $H_{c2}$ for all of the samples. The $H_{\text{irr}}$ and $H_{c2}$ properties of the C$_6$H$_8$O$_7$ added MgB$_2$ samples are significantly enhanced compared with the un-doped sample. This enhancement in $H_{\text{irr}}$ and $H_{c2}$ is a result of C substitution into B sites of the MgB$_2$ lattice. The $H_{\text{irr}}$ and $H_{c2}$ of the 10% citric acid added samples show a slight variation with sintering temperature.

Fig. 8 shows the temperature dependence of the normal state resistivity of un-doped and 10 wt% citric acid added samples sintered at 650$^\circ$C to 950$^\circ$C. The higher $\rho$ values for the 10% citric acid added MgB$_2$ samples indicate that the impurity scattering is stronger, due to the C substitution into B sites. The residual resistivity ratio (RRR) values varied with sintering temperature and are listed in Fig. 8. The transport properties of the samples are mainly dependent on the C substitution level, the grain...
crystallinity and connectivity, and the MgO impurity phase content. In our samples, the C substitution levels of the 10% citric acid added samples are almost the same, while the varied transport properties among the 10% citric acid added samples sintered at different temperatures are due to the variations in grain crystallinity and connectivity, and in the MgO impurity phase content, which are caused by different sintering temperatures.

\( C_6H_8O_7 \) in the Mg and B mixture melts at lower temperatures and decomposes at temperatures below the formation temperature of MgB\(_2\), hence producing highly reactive and fresh C on the atomic scale, as well as an assortment of gases in the reaction environment, which reduce the speed of MgB\(_2\) grain growth, leading to a lower C substitution temperature and smaller grain size. Moreover, the fact that the C substitution possibly takes place in the gaseous state leads to very uniform C doping in the MgB\(_2\) matrix, hence significantly enhances the critical current density and the upper critical field.

However, \( C_6H_8O_7 \), as a typical carbohydrate, contains a large amount of oxygen, which leads to an increase in the amount of impurity phase MgO, resulting in degradation of the transport conductivity.
4. Conclusion

C-doped MgB$_2$ samples sintered at temperatures from 650°C to 850°C were prepared using 10wt% C$_6$H$_8$O$_7$ as the C source material. A decreased lattice parameter $a$ in comparison with the undoped sample indicated that about $x = 0.03$ of C in Mg(B$_{1-x}$C$_x$)$_2$ was substituted for B. The high field $J_c$ values, as well as $H_{irr}$ and $H_{c2}$, were significantly improved in the CA added samples, with the $J_c$ reaching $10^4$ A/cm$^2$ at 5 K and 8 T, which is a factor of 9 higher than for the undoped MgB$_2$. These enhancements are attributed to the lattice distortion resulting from the incorporation of C atoms into the MgB$_2$ crystal lattice and the smaller grain size.

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