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Effect of sintering temperature on structural defects and superconducting properties in $\text{MgB}_2 + \text{C}_4\text{H}_6\text{O}_5$

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Abstract. We report a systematic study on the effect of sintering temperature on the lattice parameters, amount of carbon (C) substitution, microstructure, critical temperature (T_c), critical current density (J_c), upper critical field (H_{c2}) and irreversibility field (H_{irr}) of 10 wt% Malic acid ($\text{C}_4\text{H}_6\text{O}_5$) doped MgB_2 superconductors. All the samples were heat treated at temperatures ranging from 600 to 900 °C. With increasing the sintering temperature both the a -axis lattice parameter and T_c are decreased compared to un-doped samples, indicating that the C released from $\text{C}_4\text{H}_6\text{O}_5$ substituted into Boron (B) position resulting in the enhancement of J_c , H_{c2} and H_{irr} .

1. Introduction

The discovery of superconductivity at 39 K [1] in the MgB_2 can be applied to a cryogen-free magnet at an operating temperature of around 20 K [2]. The improvements in critical current density (J_c), upper critical field (H_{c2}) and irreversibility field (H_{irr}) have been the key topics of research efforts. Gurevich et al have reported very high H_{c2} , up to 50 T, for MgB_2 films with high resistivities [3]. They found a correlation between the resistivity and H_{c2} and showed that the remarkable H_{c2} enhancement can be explained in the framework of the two gap superconductivity in MgB_2 , which provides special opportunities for further enhancement in H_{c2} by tuning the impurity scattering. A significant enhancement in the electromagnetic properties of MgB_2 has been achieved through a doping with various forms of carbon (C). For example, the addition of SiC [4-6], C [7, 8], carbon nanotubes (CNTs) [9], carbohydrate (CH) [10] and a liquid additive, silicone oil [20] have been found to be effective in improving the J_c - H characteristics of MgB_2 . In particular, C can enter the MgB_2 structure by substituting for B, which leads to increased impurity scattering in the two-band MgB_2 , and hence significantly increases J_c and the H_{c2} . However, the C doping effect for MgB_2 superconductor has been limited by the local agglomeration of nano-sized dopant particles. In that case un-reacted C remains in the MgB_2 matrix and reacts with Mg or B powders, resulting in the formation of impurity phases. To overcome these properties, it is necessary to study the homogeneity of mixing as well as the activity of the reactions between B and C materials so as to achieve a full reaction. The various methods have been studied by many groups. Mickelson et al. [11] first reported that B_4C was considered to be one of the more reactive C-containing compounds because free C was liberated from B_4C . However, using B_4C compound meant that a higher sintering temperature up to 1200

°C was needed, as well as a longer sintering time. Dou *et al.* [12] studied the effects of SiC doping on MgB₂ superconductor to overcome the same problems. Even though SiC was much more effective at enhancing the J_c at a low sintering temperature (~650 °C), there were agglomerations of nano-particles in the MgB₂ matrix, resulting in blocking of current flow. C and CNT as dopants also require a higher sintering temperature of 900 °C for C substitution to take place. In addition, because of the high aspect ratio, the CNTs were much more easily entangled [13], reducing homogeneity.

In our group we have already shown that J_c enhancement by more than one order of magnitude in high magnetic field can be achieved with only a slight reduction in T_c for MgB₂ + C₄H₆O₅ [10] sintered at 900 °C. To further explore the potential as a C source of C₄H₆O₅, low temperature sintering also has significant advantages for commercial MgB₂ conductors such as MgB₂ + SiC. Recently, Fujii *et al.* [14] prepared Fe-containing MgB₂ tapes at low temperature of 600 °C using MgH₂ instead of Mg powder. The H_{c2} and H_{irr} enhancement at low sintering temperature is crucial for the selection of various sheath materials and reduction of production costs. For these reasons, C₄H₆O₅ is one of the main candidate materials for low sintering temperature processing at 600 °C, as this C source can be fully decomposed at temperatures as low as 300°C.

2. Experimental

MgB₂ pellets were prepared by an in-situ process with the addition of 10 wt% C₄H₆O₅. The fabrication processing of pellet and wire is described in elsewhere [10, 15]. All samples were sintered in a tube furnace at temperatures ranging from 650 to 900°C for 30 min, and at 600 °C for 4 hours under high purity argon gas. The heating rate was 5 °C/min. All samples were characterized by X-ray diffraction (XRD), field emission gun-scanning electron microscopy (FEG-SEM), T_c , H_{irr} , and H_{c2} . The lattice parameters were obtained from Rietveld refinement. T_c was defined as the onset temperature at which diamagnetic properties were observed. In addition, H_{c2} and H_{irr} were defined as $H_{c2} = 0.9R(T_c)$ and $H_{irr} = 0.1R(T_c)$ from the resistance (R) versus temperature (T) curve.

3. Result and discussion

As shown in Figure. 1, the a -axis lattice parameter decreases from 3.0851 Å for a well developed un-doped sample sintered at 900°C for 30 min to 3.0749, 3.0753, 3.0722, 3.0734, 3.0764 Å for MgB₂ + 10 wt% C₄H₆O₅ samples sintered at 600 °C for 4 hours and 650, 700, 800, and 900°C for 30 min, respectively. Even though there are some fluctuations in the changes of the a -axis lattice parameter for the samples with different sintering temperatures, the amount of C substitution seemed to be saturated in Figure. 2, with an average value of $x \sim 0.0242$ in the Mg (B_{1-x}C_x)₂, at all sintering temperatures [16]. In general, the shrinkage of the a -axis is attributed to the substitution of C for B. These results indicate that significant C substitution can be achieved for MgB₂ + 10 wt% C₄H₆O₅, even with a low sintering temperature regime. Thus the decomposition of C₄H₆O₅ produces highly reactive C, allowing it to achieve relatively higher C substitution levels at lower temperature, compared to nano-C, B₄C, and carbon nano-tube [17].

Figure. 3 shows the T_c for both doped and un-doped samples which increases with increasing sintering temperatures. This indicates that small grains and imperfect crystallinity exist in samples processed at lower temperatures. Yamamoto *et al.* [18] reported that H_{irr} can be enhanced by degradation of crystallinity due to a low temperature solid-solid reaction. That is, low crystallinity is primarily responsible for larger H_{irr} and H_{c2} . It should be noted that the T_c of MgB₂ + 10wt% C₄H₆O₅ samples are relatively lower than those of un-doped MgB₂ over the whole sintering range. This result is related to the lattice disorder due to C substitution into B sites.

Figure. 5 shows the magnetic J_c of the un-doped sample and the 10 wt% malic acid-added MgB_2 samples as a function of the heat-treatment temperatures. It can be seen that the J_c values of the un-doped sample heat-treated at 900 °C for 30 min are higher than those of the C-doped samples in a low magnetic field region at 20 K but slightly lower at 5 K. As the applied magnetic field increases, a crossover between the un-doped and doped samples exists, and the J_c values of the doped samples were much higher than those of the un-doped sample in the high field ranges, indicating an enhanced flux pinning strength. Meanwhile, it was observed that the magnetic J_c values of the doped samples did not show a significant difference among the different heat-treatment temperatures. This is because C substitution was saturated at high temperature region. Fig. 4 also shows the transport J_c at 4.2 K for un-doped and $MgB_2 + 10$ wt% $C_4H_6O_5$ wires with different heat-treatment temperatures. $MgB_2 + 10$ wt% $C_4H_6O_5$ at 600°C for 4 hrs showed the highest J_c due to poor crystallinity and C substitution.

The temperature dependence of H_{irr} and H_{c2} for all the un-doped and $MgB_2 + 10$ wt% $C_4H_6O_5$ samples sintered at different sintering temperatures are shown in Figure 6. We observed that H_{irr} and H_{c2} were depressed systematically as the sintering temperature increased to 900 °C. This indicates that degradation of crystallinity at low temperature can be the driving force for larger H_{irr} and H_{c2} , as mentioned above. In addition, the significant C substitution into B sites at a sintering temperature as low as 600 °C may induce disorder on the lattice sites, which can lead to the enhancement of the H_{irr} and H_{c2} .

Electrical resistivity (ρ) values at 40 K and 300 K and Residual resistivity ratios (RRR , $\rho_{300 K}/\rho_{40 K}$) for the un-doped and $MgB_2 + 10$ wt% $C_4H_6O_5$ samples are summarized in Table 1. The higher ρ values for the doped MgB_2 samples indicate that the impurity scattering is stronger due to a greater C substitution into the B sites [10]. As the heat-treatment temperature increased from 600 °C to 900 °C, the RRR values increased from 1.54 to 1.62. The RRR for the un-doped sample had a higher value of 2.15 than those of the $C_4H_6O_5$ doped samples representing a good crystallinity. For a polycrystalline MgB_2 , the RRR value reflects a sample's quality. This may also be related to the grain connectivity factor as well. Rowell [19] suggested that the $\Delta\rho$ ($\rho_{300 K} - \rho_{40 K}$) values are very effective in revealing a connectivity factor.

4. Conclusion

We investigated the effects of the heat-treatment temperature on the superconducting properties, structural defects, lattice parameters, actual C substitution amount, T_c , J_c , H_{c2} and H_{irr} for 10 wt% $C_4H_6O_5$ doped MgB_2 bulk and wires. With increasing the sintering temperature, both the a-axis lattice parameter and T_c are decreased compared to un-doped samples, indicating that the C released from $C_4H_6O_5$ substituted into B position resulting in the enhancement of J_c , H_{c2} and H_{irr} .

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Table 1. Measured resistivity data for un-doped MgB₂ and 10wt% C₄H₆O₅ samples with different sintering conditions.

Samples	Sintering Conditions (° C)	$\rho_{40\text{ K}}$ ($\mu\Omega\text{cm}$)	$\rho_{300\text{ K}}$ ($\mu\Omega\text{cm}$)	RRR ($\rho_{300\text{ K}}/\rho_{40\text{ K}}$)
Un-doped	650 °C × 30min	41.8	89.87	2.15
Un-doped	900 °C × 30min	24.8	52.08	2.10
MgB ₂ + C ₄ H ₆ O ₅	600 °C × 4 hrs	137.1	210.63	1.54
MgB ₂ + C ₄ H ₆ O ₅	650 °C × 30min	116.6	152.89	1.31
MgB ₂ + C ₄ H ₆ O ₅	700 °C × 30min	88.9	136.48	1.53
MgB ₂ + C ₄ H ₆ O ₅	800 °C × 30min	94.8	144.67	1.52
MgB ₂ + C ₄ H ₆ O ₅	900 °C × 30min	90.2	146.50	1.62

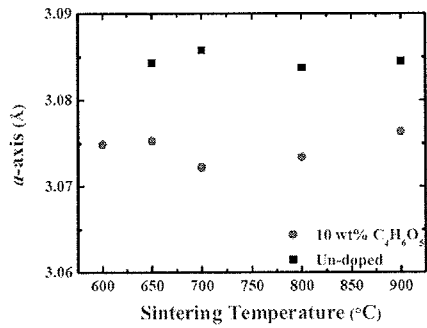


Figure 1. The a -axis lattice parameters for referenced un-doped MgB_2 sintered from 650 °C to 900 °C for 30 min and $\text{MgB}_2 + 10\text{wt}\%$ $\text{C}_4\text{H}_6\text{O}_5$ samples sintered from 600 (4 hrs) to 900 °C (30 min).

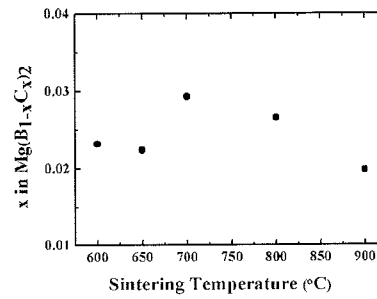


Figure 2. The amount of C substitution (x) in the $\text{Mg}(\text{B}_{1-x}\text{C}_x)_2$ for $\text{MgB}_2 + 10\text{wt}\%$ $\text{C}_4\text{H}_6\text{O}_5$ samples sintered from 600 (4 hrs) to 900 °C (30 min).

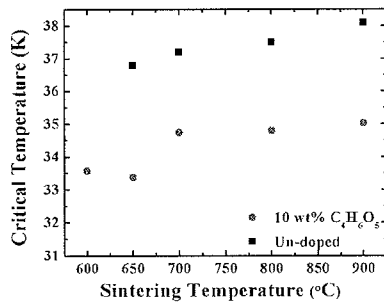


Figure 3. The T_c for referenced un-doped MgB_2 sintered from 650 °C to 900 °C for 30 min and $\text{MgB}_2 + 10\text{wt}\%$ $\text{C}_4\text{H}_6\text{O}_5$ samples sintered from 600 (4 hrs) to 900 °C (30 min).

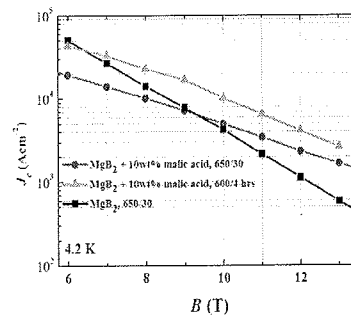


Figure 4. The transport J_c at 4.2 K for referenced un-doped MgB_2 wire sintered at 650 °C for 30 min and $\text{MgB}_2 + 10\text{wt}\%$ $\text{C}_4\text{H}_6\text{O}_5$ wires sintered at 600 (4 hrs) and 650 °C (30 min).

