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Effects of nano-carbon doping and sintering temperature on microstructure and properties of MgB_2

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ABSTRACT

We fabricated nano-carbon (NC) doped MgB_2 bulks using an in situ process in order to improve the critical current density (J_c) under a high magnetic field and evaluated the correlated effects of the doped carbon content and sintering temperature on the phase formation, microstructure and critical properties. $MgB_{2-x}C_x$ bulks with $x = 0$ and 0.05 were fabricated by pressing the powder into pellets and sintering at 800 °C, 900 °C, or 1000 °C for 30 min.

We observed that NC was an effective dopant for MgB_2 and that part of it was incorporated into the MgB_2 while the other part remained (undoped), which reduced the grain size. The actual C content was estimated to be 68–90% of the nominal content. The NC doped samples exhibited lower T_c values and better J_c(B) behavior than the undoped samples. The doped sample sintered at 900 °C showed the highest J_c value due to its high doping level, small amount of second phase, and fine grains. On the other hand, the J_c was decreased at a sintering temperature of 1000 °C as a result of the formation of MgB_4 phase.

1. Introduction

The discovery of MgB_2 superconductor has opened the door to applications at temperatures and magnetic fields unattainable by conventional superconductors, due to its various attractive characteristics, such as its high critical temperature (T_c), weak-link free grain coupling, and low material cost. However, MgB_2 has poor grain connectivity and a lack of pinning centers, which result in a rapid decrease in its critical current density (J_c) value at high magnetic fields compared to conventional Nb-based superconductors, and this poor J_c(B) behavior needs to be improved for the practical application of this material.

In order to improve its J_c performance under magnetic fields, J_c(B), the enhancement of the upper critical field (H_{c2}) and introduction of flux pinning centers have been attempted by various methods. As a simple and practical method, chemical doping seems to be a promising technique for improving the J_c(B). Specially, carbon-containing precursors such as SiC, graphite, nano-carbon (NC), and carbon nanotubes (CNTs) were found to be effective for the enhancement of the irreversibility field (H_{irr}) and J_c(B), because the substitution of C into the B sites leads to intra-band scattering that increases the H_{c2}, as reported by many groups [1–4]. Among these precursors, we considered that NC (amorphous carbon) would be an attractive dopant, because of its nano size and low decomposition temperature (150–700 °C) and cost.

In our previous study, we selected NC as a dopant and evaluated the effect of the nominal NC content on the critical properties [3]. However, the relation between the doping effect and sintering temperature, actual C content, and NC microstructure remained unclear. In a systematic extension to our previous study, therefore, we fabricated $MgB_{2-x}C_x$ ($x = 0$ and 0.05) bulk samples and evaluated the effect of the doping and sintering temperature on the phase formation, microstructure, degree of doping, and critical properties.

2. Experimental procedure

The bulk MgB_2 superconductors were prepared using a conventional powder metallurgy technique through an in situ reaction. Magnesium (Tangshan 325 mesh, 99.9%), amorphous Boron (Tangshan, 99.9%), and NC (99%, diameter of 5–30 nm) were mixed, compacted, and sintered at 800 °C, 900 °C, or 1000 °C for 30 min in an Ar atmosphere. The nominal compositions were $MgB_{2-x}C_x$ with

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x = 0 and 0.05 and the sintered samples had dimensions of 10 mm in diameter and 1.5 mm in thickness. A detailed explanation of the fabrication procedure was given in Ref. [3]. The undoped and NC-doped MgB_2 bulks sintered at 800 °C, 900 °C, and 1000 °C are hereafter denoted as the undoped-800, -900, and -1000 samples and the doped-800, -900, and -1000 samples, respectively.

The crystalline structure and phase formation were examined by powder X-ray diffraction (XRD) using a BRUKER (D8 Discover) diffractometer with Cu Kα radiation. The change in the lattice parameters was calculated from all of the MgB_2 peaks and confirmed using the EVA® program based on Rietveld refinement analysis. The microstructure was observed by transmission electron microscopy (TEM). The magnetic J_c and T_c values were derived from the height of the magnetization loop using Bean's model. The magnetization of the samples was measured at 5 K using a magnetic property measurement system (MPMS, Quantum design) in a time-varying magnetic field and amplitudes of up to 5 T.

3. Results and discussion

Fig. 1 shows the XRD patterns of the undoped and doped samples. We observed that the XRD patterns did not show any distinguishable difference between the doped and undoped samples at the same temperature, but revealed significant dependence on the sintering temperature. For both the undoped and doped samples sintered at 800 °C and 900 °C, the XRD patterns were similar to one another and showed MgB_2 as the major phase and MgB_4 and MgO as secondary phases. On the other hand, for the undoped-1000 and doped-1000 samples, the MgB_2 peak intensities decreased, while the MgB_4 intensities increased significantly, indicating that a sintering temperature of 1000 °C is too high to form MgB_2. In general, it is known that the vapor pressure of Mg is 4.40 mmHg, 7.58 mmHg, and 11.96 mmHg at 800 °C, 900 °C, and 1000 °C, respectively [5]. Thus, Mg evaporates more severely at higher temperature, causing the formation of a greater amount of the Mg deficient phase, MgB_4, at 1000 °C. In addition, no carbon related peak was observed in the XRD pattern of the doped samples, probably because the NC size was too small to be detected by XRD.

From the XRD patterns, we calculated the MgB_2 grain size using the Williamson-Hall equation by measuring the full width at half maximum (FWHM) of the MgB_2 (1 0 1) peaks, as shown in Fig. 2. For both the undoped and doped samples, the FWHM values decreased as the sintering temperature increased, moreover the values of the doped samples are larger than those of the undoped samples at the same sintering temperatures. The grain size of the undoped-800, -900, and -1000 samples are calculated to be 0.65 μm, 0.71 μm, and 0.73 μm, and the corresponding values for the doped samples are 0.61 μm, 0.63 μm, and 0.71 μm, respectively. The grain size increased as the sintering temperature increased for both samples and the doped samples had a slightly smaller grain size than the undoped samples at the same sintering temperature. We considered that the remaining NC, which was not incorporated into the MgB_2 lattice, restricted the grain growth of MgB_2 during the sintering process, and the evidence of remaining NC particles will be presented later. It is known that a small grain size has a beneficial effect on the flux pinning, because the grain boundary effectively acts as a pinning site in MgB_2.

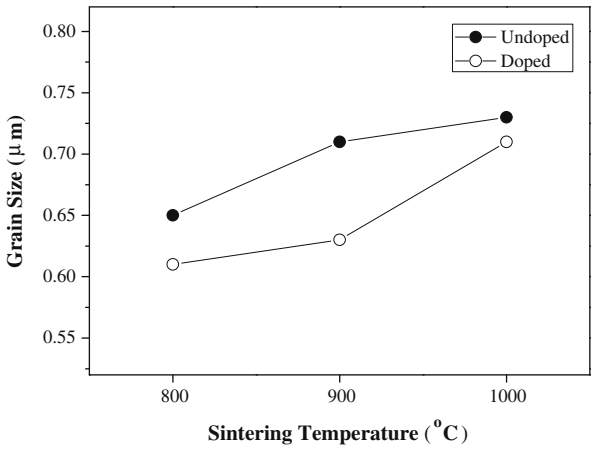

Fig. 2. Dependence of FWHM of (1 0 1) peak and grain size on sintering temperature.

The a- and c-axis lattice parameters of MgB_2 were measured in order to analyze the doping content of NC. From the magnified XRD patterns in Fig. 1, we observed that the 2θ values of the (1 0 0) peak were 33.59°, 33.60°, and 33.59° for the undoped-800, -900, and -1000 samples and 33.66°, 33.72°, and 33.71° for the doped-800, -900, and -1000 samples, respectively, and that the 2θ values of the (0 0 2) peak were in the range of 51.88–51.96° for all of the samples. Using Rietveld refinement analysis via the EVA® program, the lattice parameters of all of the samples were obtained and presented in Fig. 3. The a-axis lattice parameters for the doped-800, -900, and -1000 samples were 3.0765 Å, 3.0730 Å, and 3.0731 Å, respectively: the a-axis lattice parameter decreased as the sintering temperature increased to 900 °C and then remained unchanged at 1000 °C. The a-axis lattice parameter of the undoped samples did not vary with the sintering temperature (3.0871–3.0872 Å). In addition, the c-axis lattice parameters for all of the samples remained almost constant within the margin of error, being in the

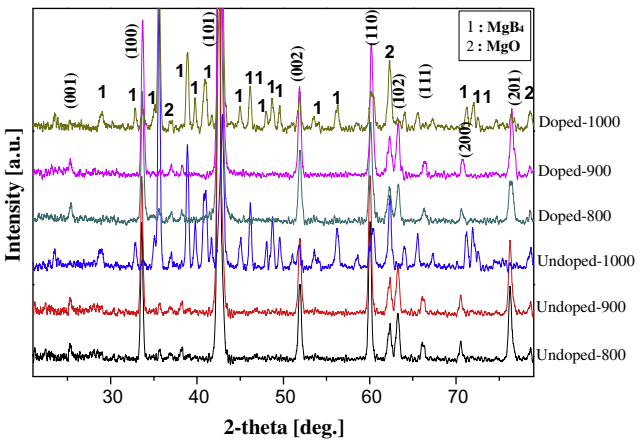

Fig. 1. (a) XRD patterns of the undoped and doped samples.

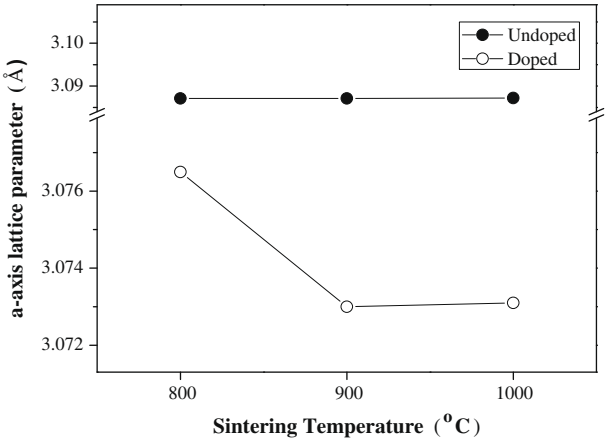

Fig. 3. Variations of the a- and c-axis lattice parameters of MgB_2 with the sintering temperature.