X-ray absorption spectroscopic study of a hot pressed MgB_2

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Abstract

X-ray near edge absorption spectra (XANES) of boron and oxygen K edge of a hot-pressed MgB_2 (HP2) sample were measured by using synchrotron radiation. The HP2 was produced by annealing a commercial powder of MgB_2 in ambient air under a hydrostatic pressure of 2.0 GPa at 900 °C. No substantial change of the electronic structure in HP2 was observed as indicated in the B K-edge XANES. This sample maintains high superconductivity and enhances the critical current density. The XANES and the XRD combined indicate that both MgO and B_2O_3 in HP2 increase and more B_2O_3 than MgO was produced during the hot-press process. The better connection of the grain in HP2 can be the major cause to increase its critical current density. However, the impurity may also increase the flux pinning and therefore increases the current density.

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1. Introduction

Since, the discovery of superconductivity in MgB_2 [1], the possibility of using it for industry applications due to its simple chemical form and relatively high superconducting transition temperature, in making superconducting magnets and electronic devices attract many of scientists to investigate the detail properties of this intriguing material. A high critical current density in high magnetic fields is a useful property. The critical current density of MgB_2 was found relevant to the defect/impurity and the inter-grain interconnectivity in the material. Defects can be generated by nano-particles doping [2,3], chemical doping [4,5], and particle irradiation [6]. These defects can act as effective flux-pinning centers which capture the vortices. The superconducting current dissipation will occur only when the force exerted on the vortices is strong enough to overcome the barrier which prevents vortices to

move, and therefore, the current can be sustained in the sample without dissipation.

A better inter-grain interconnectivity in the material can be achieved by sintering the sample under high pressure to improve the microstructure of the sample [7]. Besides that there is a report showed that a hot-pressed MgB_2 had dispersed MgO and dislocations, which may act as flux-pinning centers [8]. There are other reports showed that the defects of the hot-pressed MgB_2 powder annealing under a high pressure include small angle twisting, tilting and bending boundaries [9,10].

For further understanding the hot-pressed MgB_2 , we conduct a study of MgB_2 powder annealing under a high pressure in ambient air. In this work, we report our results of MgB_2 powder annealing under a high pressure of 2.0 GPa at 900 °C. The hysteresis curves were measured at various temperatures to determine the critical current densities. About an order of magnitude increase in the critical current was found. The electronic structure was investigated by X-ray absorption spectroscopy. No significant change of the electronic structure was observed. However, both the impurity of MgO and B_2O_3 was observed to increase and more B_2O_3 than MgO was produced during the hot-press process.

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2. Sample preparation and characterization

In producing a hot-press MgB_2 sample, commercial MgB_2 powders (-325 mesh, 99.9%) were pressed into a small pellet with a dimension of 5 mm in diameter and 3 mm in thickness. The pellet was packed into a platinum tube and both ends of the tube were sealed. The tube was fixed in a graphite furnace for annealing at 700, 900, and 1200 °C under a high pressure. The hot-press instrument used here is called quick-press piston cylinder that was manufactured by the depth of the Earth Company in USA. The sample was heated to the desired temperature under high pressure at the rate of 30 °C/min. and was finally quenched below 60 °C in 1 min when the desired temperature was reached. The pressure was kept during the quench. One of the sample was heated to 700 °C under 1.0 GPa and maintain at 700 °C for 10 min. The other two samples were heated, respectively, to 900 and 1200 °C and quenched. The last one (1200 °C one) was found no phase of MgB_2 and thus we show characteristics of the samples with the annealing temperatures up to 700, and 900 °C (hereafter we referred the one at 700 °C as HP1, and the one at 900 °C as HP2) by using X-ray powder diffraction (XRD) patterns and zero-field cooling susceptibility curves (obtained by a SQUID).

Fig. 1 shows the XRD patterns of a sample of the untreated MgB_2 commercial powders (hereafter it was referred as MgB_2 powder) and the HP1, and HP2 samples. The peaks marked with asteroids result from silicon powders that we put on the surface of the samples for angle calibration. There are no substantial impurity phases shown in HP samples, except small peaks of MgO indicating small amount of MgO existing in the HP samples. The zero-field cooling curves of susceptibility at 30 oersteds are shown in Fig. 2. The critical transition temperatures of these samples as derived from these curves are shown in Table 1. The critical transition temperature of both HP samples decreases a little, but the transition width is observed smaller for HP2 than that of MgB_2 powder. Besides, the superconducting volume looks also better in HP samples than in MgB_2 , indicating better inter-grain connections in HP samples, especially for HP2 sample. Since HP2 exhibits much better quality than the MgB_2 powder in terms of its

Fig. 1. The X-ray powder diffraction patterns of the samples of MgB_2 powder, HP1, and HP2. The peaks marked by '*' are the calibration peaks from Si powders.

Fig. 2. The zero-field cooling magnetization curves of the samples of MgB_2 , HP1, and HP2 measured by a SQUID at 30 oersteds.

superconducting volume and the transition width, in the following studies we compare the HP2 and the MgB_2 powder only.

3. Determination of the critical current density

The curves of magnetization versus applied field (the hysteresis loop) were measured for both MgB_2 powder and HP2 at various temperatures by a SQUID in the magnetic field range of -50 and $+50$ kOe. The critical current density was calculated from the hysteresis loops by applying the Bean model. In the measurements a disk of 4.35 mm in diameter was used. The apparent density of HP2 was found to be 2.39 g/cm^3 close to the density of the MgB_2 crystal (2.63 g/cm^3), while the apparent density of MgB_2 powder disk was 1.71 g/cm^3 . Fig. 3 shows the hysteresis loops of the samples at 10, 20 and 30 K. The dependence of the critical current density J_c on the applied magnetic field was derived at these temperatures by using a formula, $J_c = 30\Delta M/d$, according to the Bean model [11], where ΔM is the difference of the magnetization, in the unit of emu per cubic centimeter, between the decrease and the increase in the magnetic field, and d is the diameter of the sample in the unit of centimeter. As shown in Fig. 4, the values of the critical current densities J_c of HP2 at various temperatures are always about an order of magnitude higher than those of MgB_2 . The decrease rate of J_c with increase in the field is also much slower for HP2. It is clear that the J_c of HP2 sample is improved as compared to the untreated MgB_2 powders. The flux jumps were observed in HP2 at 10 K (Fig. 3) below the magnetic field of about 1 T [12]. No critical density was determined in that region.

4. The X-ray absorption near-edge spectroscopy (XANES) measurement of the B K-edge

The X-ray near-edge absorption spectra were obtained by using the high-energy spherical-grating monochromator (HSGM) beamline at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan, ROC. The X-ray total fluorescence yields (TFY) was detected by a multi-channel plate (MCP) for the sample's K-edge of boron. The drain current of the sample that records the total electron yields (TEY) was also recorded to monitor the surface

Table 1

Characteristics of samples; the superconducting transition temperature, T_c , and the transition width were measured from the zero-field-cooled susceptibility curves (Fig. 2), while the lattice constants were derived from the XRD data (Fig. 1)

Samples	Annealing condition	T_c (K)	Transition width (K)	Lattice constants (Å)	
				a	c
MgB ₂	Powder (Alfa Aesar)	38.4	1.8	3.083(1)	3.519(1)
HP1	700 °C, 1.0 GPa	38.2	2.6	3.090(3)	3.524(5)
HP2	900 °C, 2.0 GPa	38.3	1.5	3.086(2)	3.524(3)

The numbers in the parentheses are the errors for the last digital.

contaminations. A 400 mm^{-1} spherical grating was used. Both the widths of the entrance and the exit slits were set to be $30 \mu\text{m}$. The photon energy resolution of this setting was estimated to be about 0.10 eV . Both samples of MgB₂ powder and HP2 had been polished before put into the vacuum chamber for the measurement.

Fig. 5 shows the results of XANES of boron K-edge. The spectra had been normalized such that the spectral areas in the energy range of 185 and 210 eV, by exclusion the area under the B₂O₃ peak at about 193.8 eV, were the same. By this way, the influence of B₂O₃ in the sample was reduced substantially in this normalization procedure, especially in the region near the threshold. The peak A is interpreted to result from the transition to the unfilled p states cross over the Fermi level [13,14], while the peak B may result from the resonant elastic scattering [13] and related to the surface contaminations [15]. The peak C indicates the contamination of the B₂O₃, since the position of this peak matches that of B₂O₃ powders very well. It appears that the peak C is enhanced in the sample HP2, indicating the increase in contamination of B₂O₃ in HP2. This

contamination is in the bulk rather than in the surface since the TEY spectrum (not shown) gave about the same intensity of this peak for both MgB₂ powder and HP2, indicating that surface contamination of B₂O₃ was about the same for both samples. However, the intensity of the peak B is reduced in the HP2 sample. The polish of the samples seems more effectively to remove some of the surface contaminations in HP2 than in MgB₂ powder.

The intensity of the peak A in HP2 is deviated little from that in MgB₂ powder, although more contaminations of B₂O₃ was found in HP2. It appears that the hole states in the valence band at the Fermi energy in HP2 has no substantial change. This indicates that the electronic structure, especially in the boron plane of MgB₂, has little change for HP2 sample.

In order to investigate further the impurity of the oxides in the sample, the oxygen K-edge XANES was measured. In this measurement, a spherical grating with 1200 mm^{-1} grooves was used and the energy resolution of the photon beam was estimated to be about 0.25 eV . The normalized O K-edge XANES of HP2 and MgB₂ powders are shown in Fig. 6. The spectra of MgO and B₂O₃ are also shown for comparisons. In MgB₂ powders, we observe peak A, B and C resembling those in MgO, but such peaks are relatively not so pronounced in HP2. However, the characteristic peaks of D and E resembling those of B₂O₃ is more distinguishable in HP2 than in MgB₂ powders, indicating the increase in B₂O₃ for HP2 sample, in consistent with the observation in the B K-edge XANES (Fig. 5) that also indicates the increase in B₂O₃. The ratio of the amount of MgO and B₂O₃ was apparently reversed in HP2 as compared to MgB₂ powder. In combination with the XRD measurement (Fig. 1) that indicates the increase in MgO in HP2, one concludes that both MgO and B₂O₃ increase in HP2 but more B₂O₃ are produced under the hot-press process. Since,

Fig. 3. The hysteresis loops of (a) MgB₂ powders and (b) HP2 at temperatures 10, 20 and 30 K in the field range of -50 and $+50 \text{ kOe}$.

Fig. 4. The critical current densities of MgB₂ powder (open dots) and HP2 (full solid dots) derived from Fig. 3 by using Bean model.

Fig. 5. The B K-edge XANES of MgB_2 powders (dash lines) and HP2 (solid lines).

Fig. 6. The O K-edge XANES of MgB_2 powders and HP2. Those of MgO and B_2O_3 are also shown for comparisons.

the signal of B_2O_3 in the XRD pattern is very weak, it comes no surprise that there is no signal appears in the HP2 sample in the XRD measurement.

5. Summary

The hot-press process in the ambient air appears to enhance the critical current density as well as the connection of the grains. The impurities of MgO and B_2O_3 were observed to increase, more B_2O_3 than MgO was produced during the hot-press process. No substantial change of the electronic structure in HP2 was observed. The better connection of the grain in HP2 can be the major cause to increase its critical current density. However, the impurity may also increase the flux pinning and therefore increases the current density.

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