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Research paper

The reduction of optimal heat treatment temperature and critical current density enhancement of ex situ processed MgB_2 tapes using ball milled filling powder

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ABSTRACT

The optimal heat treatment temperature (T_{opt}) at which best performance in the critical current density (J_c) property at 4.2 K is obtained is influenced by the quality or reactivity of the filling powder in ex situ processed MgB_2 tapes. Using a controlled fabrication process, the T_{opt} decreases to 705–735 °C, which is lower than previously reported by more than 50 °C. The T_{opt} decrease is effective to suppress both the decomposition of MgB_2 and hence the formation of impurities such as MgB_4, and the growth of crystallite size which decreases upper critical filed (H_{c2}). These bring about the J_c improvement and the J_c value at 4.2 K and 10 T reaches 250 A/mm^2. The milling process also decreases the critical temperature (T_c) below 30 K. The milled powder is easily contaminated in air and thus, the J_c property of the contaminated tapes degrades severely. The contamination can raise the T_{opt} by more than 50 °C, which is probably due to the increased sintering temperature required against contaminated surface layer around the grains acting as a barrier.

1. Introduction

Since the discovery of superconductivity in MgB_2 [1], this material has been developed as a substitute for Nb–Ti in such applications as cryocooled systems [2,3]. As a fabrication process for the conductor, the powder-in-tube (PIT) technique, in situ and ex situ processes, has been widely adopted [4,5]. Alternatively, the internal Mg diffusion (IMD) process has been developed [6–8], which uses a Mg rod and B powder.

Among these three processes, the conductors fabricated through the IMD and in situ processes show relatively strong grain connectivity. In spite of poor packing density of the core in these conductors, the critical current density (J_c) property of the conductors is superior to that of the conductor through the ex situ process. The poor J_c property in ex situ processed conductors is mainly attributed to the weak grain connectivity. The surfaces of the filling powders for these three processes are gradually contaminated in air, by oxygen and moisture. The contaminated surface layer acts as an obstacle during sintering or reaction to the superconducting phase and results in weak connectivity of grains and hence poor J_c [9–11]. This effect is more significant in the ex situ process. Nevertheless the ex situ process still has the advantage in a high density of the MgB_2 layer over the other two processes [12]. The poor packing density in the in situ process in the same PIT technique is ascribed to the formation process of MgB_2 and hence hardly overcome. When using Mg and B powders as starting filling powder, the formation of MgB_2 causes the volume reduction of nearly 30%.

Fabrication of PIT-processed MgB_2 wires and tapes using ball milled filling powders has been extensively studied for both in situ and ex situ processes so far, and the J_c properties of these conductors have been improved. The ball milling process causes grain refinement and hence increases the density of the grain boundary which increases the pinning force [13–18]. The milling process causes the reduction of the crystallite size as well, which increases the scattering of electrons and thus reduces the mean free path which enhances upper critical field (H_{c2}) and the resistivity [19].

The influence of the milling energy on the filling powder was studied systematically with the milling rotation speed up to 360 rpm for the ex situ processed wires and tapes [20]. The optimal milling conditions under which best performance in the J_c property is obtained for the tape samples using milling powders were 144 h at 180 rpm and 36 h at 300 rpm. For these conditions, the size of grains and crystallites is comparable. Further milling deteriorates the J_c properties of the tapes. The J_c values at 4.2 K of tapes using these milled powders reach 50–100 A/mm^2 in 10 T when heat treated at 850–950 °C [17,21]. These

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J_c values are still smaller than those obtained for the in-situ processed conductors using ball milled filling powder, 270 A/mm^2 by heat treatment at 600 °C for 3 h [15].

The fresh and reactive surface of MgB_2 grains which can improve the grain connectivity in the ex situ process is created through a ball milling process [22]. These high reactive grains are also contaminated in air easily. Thus, the deterioration of the grain connectivity can take place [23]. The J_c property of the conductors is scattered widely and degrade, unless the powder is preserved and handled properly. Recently we reported the J_c improvement in the ex situ processed tapes using reactive ball milled filling powders and a controlled fabrication process [24]. The J_c value reaches about 180 A/mm^2 at 4.2 K and 10 T when milled at 500 rpm for 10 h. This value is nearly twice as large as the previously reported value, 100 A/mm^2 [17], as mentioned above. Furthermore, the optimal heat treatment temperature (T_{opt}) at which best performance in the J_c property at 4.2 K and 10 T is obtained decreases to 780 °C.

The milling energy is considered proportional to the square or the cube of milling rotation speed [20,18] and thus, the increase of the speed effectively increases the energy, compared with other parameters such as milling time. The milling energy is linear-proportional to the milling time. The milling energy of 500 rpm for 10 h was comparable to that of 350 rpm for 30 h in the previous report [24]. However, the J_c property of the tapes using the powders prepared under the latter milling condition was inferior to that under the former. In this paper we systematically prepared MgB_2 filling powders ball milled at rotation speeds up to 500 rpm for a duration up to 500 h and studied the effect of milling energy and contamination on the transport J_c properties of ex situ processed MgB_2 tapes.

2. Experimental details

MgB_2 powder (Aldrich; 99% in purity; 100 mesh) was put in WC jar and balls, and then ball milled at speeds of 150, 350 and 500 rpm for up to 500 h. The mass ratio of the balls to the sample (r_{bs}) was fixed, 46, except for 500 rpm. For 500 rpm, in order to study the effect of the r_{bs}, another r_{bs}, 18, was chosen as well. These milled powders were handled and preserved in a glove box with an Ar gas circulation system. The O_2 concentration in the box was below 1 ppm. The milling energy transferred to the powder sample for each milling condition was calculated from the method used previously [18]. Table 1 lists the milling energy per mass of the powder sample E_t/m for these milling conditions.

The as-received and milled powders were packed into a Fe tube with an outer diameter of 6.35 mm and an inner diameter of 3.5 mm and subsequently sealed in the glove box. Then, they were deformed into a rectangular-shaped tape, with a width of 4.5 mm and a thickness of 0.35 mm, by means of groove rolling and flat rolling machines. Subsequently they were heat treated at 615–945 °C for 1 h in a flow of Ar gas. These as-rolled tapes were handled and preserved in the glove box as well and exposed to air for as short a time as possible during the fabrication process to prevent contamination. However, some as-rolled tape samples with a length of 50 mm were exposed to air for 0.5–24 h on purpose to study the effect of contamination. These tapes are denoted by clean and contaminated, respectively, later.

Table 1
High-energy ball milled sample specification and the milling energy per mass of the sample E_t/m.

Ball to sample ratio r_{bs}	Rotation speed (rpm)	Milling time (h)	E_t/m (J/kg)
46	150	10	9.6×10^6
46	150	30	2.9×10^7
46	350	10	1.2×10^8
46	350	30	3.7×10^8
46	350	50	6.1×10^8
46	350	100	1.2×10^9
46	350	300	3.7×10^9
46	350	500	6.1×10^9
46	500	2	7.1×10^7
46	500	10	3.6×10^8
46	500	15	5.3×10^8
46	500	30	1.1×10^9
18	500	10	1.4×10^8
18	500	15	2.1×10^8
18	500	30	4.3×10^8
18	500	50	7.1×10^8
18	500	70	1.0×10^9

Chemical analyses on the milled powders were carried out by inductively coupled plasma (ICP) - optical emission spectroscopy (OES) with an Agilent 720-ES. The analyses were performed twice for the same powder to check reproducibility. Phase identification of the as-milled powder samples was carried out by an X-ray diffraction (XRD) method with a Rigaku RINT-TTR III X-ray diffractometer with Cu Kα radiation. The XRD data analyses were carried out with integrated X-ray powder diffraction software PDXL. The microstructural observation of the as-milled powder and tape samples was performed with a Hitachi SU-70 scanning electron microscope (SEM). The morphology and electron diffraction (ED) patterns were recorded for the as-milled powder samples with a JEOL JEM-2000EX transmission electron microscope (TEM). The samples were dispersed in CCl_4 and transferred to carbon-coated copper grids. The SEM and TEM specimens of the as-milled powders were quickly transferred into the microscopes to prevent the contamination as far as possible.

The temperature dependence of the direct-current (dc) magnetization was measured for the heat-treated tape samples above 5 K in a magnetic field of 10 Oe in a zero-field-cooling (ZFC) mode by means of a Quantum Design MPMS XL superconducting quantum interference device (SQUID) magnetometer. The measurements were carried out for the samples after peeling off the Fe sheath. The magnetic fields were applied perpendicularly to the tape surface. The magnetic critical temperature (T_c) was defined as the onset temperature at which a diamagnetic signal was observed.

Resistive measurements were performed for a piece of the MgB_2 core picked up from the Fe-sheathed tape samples using a measuring current of 1 mA by the conventional four-probe method from room temperature to 5 K in magnetic fields up to 5 T applied parallel to the tape surface. The cores were picked up by removing the Fe sheaths mechanically. The sample dimensions for the measurements were 6–8 mm × 2.0–2.5 mm × 0.18 mm. The resistive T_c and H_{c2} values were taken at 90% of the transition, whereas the irreversibility field (H_{irr}) was taken at 10% [17]. Transport critical current (I_c) measurement of the tape samples was carried out at 4.2 K and in fields up to 12 T applied parallel to the tape surface. The I_c criterion was 1 μV/cm. Multiple tape samples were prepared for the I_c measurement to check reproducibility since the transport J_c property of the tape samples is easily scattered by contamination.

3. Results and discussion

3.1. Milled powder samples

Fig. 1 shows XRD patterns of powder in the as-received state and milled at 150, 350 and 500 rpm for up to 500 h with r_{bs} = 18 and 46. The as-received powder contained some impurities such as MgO and MgB_4 [24]. With increasing the milling time, the XRD peaks assigned to MgB_2 and the impurities became broader and less appreciable, respectively. Furthermore, the MgB_2 peak shift was observed. Although the peak position was not so clear due to the broadening of the peaks, the shift suggests both the contraction of the *a*-axis and the elongation of the *c*-axis.

For r_{bs} = 46, (b)–(h), the MgB_2 peaks of the sample are very broad when the powders were milled at 500 rpm for a duration not less than 10 h. Similarly broadened MgB_2 peaks are observed for the powders milled at 350 rpm for not less than 100 h. This is in contrast to the