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Properties of MgB_2 superconductor chemically treated by acetic acid

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ABSTRACT

Commercial Alfa Aesar MgB_2 powder was chemically treated by acetic acid with the aim of MgO removing. Single-core MgB_2/Fe ex situ wires have been made by powder-in-tube (PIT) process using the powders treated with different acid concentration. All samples were annealed in argon at 950 °C/0.5 h. Differences in transition temperatures and critical currents of acetic acid treated MgB_2 are related to the normal state resistivity, effective carbon substitution from the organic solvent and the active area fraction (grain-connectivity).

1. Introduction

Several attempts have been made for ex situ MgB_2 wires by powder-in-tube (PIT) process [1–5]. Strong affinity of magnesium to oxygen leads to creation of MgO, which is limiting the inter-grain currents. MgO is present inside the MgB_2 powder in the form of small crystallites and/or amorphous state (thin layer not detectable by XRD). Some volume of fine-crystalline (comparable to the coherence length) and uniformly distributed MgO can be beneficial for the transport current property of MgB_2 due to improvement of pinning through the small normal particles [4]. On the other side, clean grain boundaries are very important for the currents flow in MgB_2 filaments, since dirty grain boundaries potentially reduce the critical currents. Several insulating phases were found at the grain boundaries, consisting of MgO, boron oxides or boron carbide [6], which should be minimized for high current density conductors. Fujii et al. have presented the positive effect of chemically treated MgB_2 powder by a benzene solution of 0.2 M benzoic acid, which promotes the substitution of carbon from the solvent by the removal of the surface MgO layers [7].

The aim of this contribution is to show the effect chemical treatment by acetic acid on the transport current properties of ex situ MgB_2/Fe wires.

2. Experimental

Acetic acid was initially tested for pure MgO powder and due to its effective etching it was used for chemical treatment of commercial (Alfa Aesar) MgB_2 powder. As-received Alfa Aesar powder (A0) was soaked in the solution of acetic acid of different concentration 0.3–10 vol.% mixed with Toluene and the samples were named by A1–A4, see two left columns in Table 1. Ultrasonic assistance was applied for chemical treatments with the same duration of 20 min. Chemical reaction, which take place between acid and MgO is expressed by the following equation:

$$2CH_3COOH + MgO \rightarrow (CH_3COO)_2Mg + H_2O$$

After reaction the powders were filtered at decreased pressure and washed in solvent to remove $(CH_3COO)_2Mg$. The solvent was then dried by heating up in low pressure argon atmosphere. Chemically treated powders were analyzed by transmission infra-red spectroscopy using FT-IR Nicolet MAGNA 750 spectrometer.

Fe tubes of 6/4 mm were filled by powders A0–A4 and deformed into a rectangular wires 1.20 × 1.20 mm^2 by two-axial rolling. All wire samples were finally heat-treated at 950 °C for 0.5 h in Ar gas. Optical microscope Olympus BX51M was applied for observation of MgB_2 cores. Critical currents (at 1 $\mu V\,cm^{-1}$) were measured in the scale of external magnetic field ranging to 9 T at liquid helium temperature. Resistive four-probe measurement with the constant DC of 100 mA was used for $R(T)$ measurement of MgB_2 cores extracted from iron sheath. X-ray analysis was used for powdered extracted MgB_2 cores A0–A4.

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Table 1
Acetic acid treated samples and their irreversibility fields estimated by the current density level 100 A/cm^2 and by Kramer's plot.

Sample	Acetic acid concentration (vol.%)	B_{irr} (100 A/cm^2, T)	B_{irr} ($I_c^{1/2} \times B^{1/4}$, T)	ΔB_{irr} (T)
A0	0	8.0	9.5	1.5
A1	0.3	9.5	10.5	1.0
A2	2.5	11	11.25	0.25
A3	5	9.7	11.5	1.8
A4	10	7.5	11	3.5

3. Results and discussion

Fig. 1 shows 2Θ scans of powders: as-received A0 and treated by 10 vol.% of acetic acid A4. It is apparent that the treatment by acetic acid has dissolved the crystalline part of MgO (220), which gives an assumption that MgO from MgB_2 grains is removed. As it was already shown, the structure of Alfa Aesar MgB_2 powder is not uniform containing particles ranging for sub micrometer size up to 100 µm [8]. It was found that MgB_2 particle-size refinement take place especially for high concentration of acetic acid. Fig. 2 shows the cross-sections of as-deformed wires containing powders treated by different concentration of acetic acid (A0, A4 and powder treated by 99.8% acetic acid). Averaged particle size was estimated by software analysis of cross-sections in Fig. 2a–c observed by polarized light optical microscopy (POM). SEM pictures of two powders used for wires A0 and A4 are shown in Fig. 2d and e. Fig. 2f compares the particles size obtained by POM together with the crystalline size of annealed samples A0–A4 estimated by X-ray analysis, see Table 3. It is evident, that particle size and crystalline size are decreasing similarly with increased acid concentration. This suggests the penetration of acetic acids through the sub-grain boundaries and decomposition of big MgB_2 particles into small ones ("*chemical milling*").

Fig. 3 shows the infra-red spectra made for powders treated by acetic acid where the creation of magnesium acetate is expected. Therefore, it is necessary to focus on the couple of absorption bands, which are typical for stretching vibrations of COO^- group. Characteristic adsorption bands at 1560 cm^{-1} and 1415 cm^{-1} correspond to antisymmetrical and symmetrical stretching vibrations of COO^- group – belong to aliphatic carboxylic acid salt. One can see that the intensity corresponding to carboxylic acid salt is decreasing with decreased acid concentration (see dotted lines).

Fig. 4a presents critical currents for the wires made of powders A0–A4. It is apparent that the slope of $I_c(B)$ as well as absolute values of I_c are strongly influenced by the acid concentration. Increasing I_c are correlating with decreased acid concentration, which leads to cross over of $I_c(B)$ with the A0 wire characteristic at lower and lower field (8.5 T → 5.5 T). Less sloping $I_c(B)$ characteristic can be accounted to the particle-size refinement [7] and lowered I_c magnitudes to more dirty grain boundaries worsening the inter-grain-connectivity.

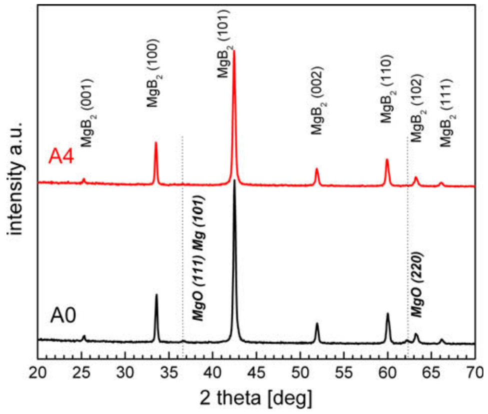

Fig. 1. X-ray scans for Alfa Aesar MgB_2 powder A0 and chemically treated powders A4.

Only wire A1 treated with 0.3 vol.% of acetic acid shows higher I_c than for A0 in the whole field region (3.5–8.5 T). On the other side, the slope of $I_c(B)$ for A1 is not so moderate as for all more intensively treated samples. It is interesting that the shape of $I_c(B)$ is more or less the same for A2–A4, but the absolute value of I_c is sensitive to acid concentration and removal of organic solvent [7]. The crystalline size (see Table 3) and particle-size refinement (Fig. 2f) among A2–A4 are not considerably different, which may be responsible for similar $I_c(B)$ slopes. It is expected that not removed $(CH_3COO)_2Mg$ is most probably converted into MgO and CO_2 during the heat treatment at 950 °C [9]. Instead of, not removed organic solvent can be a source of carbon for partial substitution of boron atoms, which increases the upper critical field and consequently changes the slope of $I_c(B)$ dependence. While around 6 times increased I_c was measured for A1 at 8 T, one order of magnitude I_c improvement is shown for less clean sample A2 at the same field.

Critical current data were used for estimation of the irreversibility field B_{irr}, which was determined using an extrapolation of J_c versus B to 100 A/cm^2 and by Kramer's plot $I_c^{1/2} \times B^{1/4}$ versus B to 0 shown in Fig. 4b. While the samples A2–A4 have a linear shows $I_c^{1/2} \times B^{1/4}$ dependences allowing the linear extrapolation to $B_{irr} = 11–11.5$ T, wires containing the most pure powders (A0 and A1) show not linear dependences at higher fields ($B > 6$ T) and B_{irr} estimation is more difficult and giving $B_{irr} = 9.5–10.5$ T. The observed linear $I_c^{1/2} \times B^{1/4}$ dependences for more contaminated MgB_2 samples is not yet understood. Table 1 summarizes the values of B_{irr} estimated by mentioned extrapolations and their differences. Generally, the values obtained by J_c versus extrapolation to 100 A/cm^2 are lower than by Kramer's plot ($B_{irr} = 0.25–3.5$ T). There is an open question which extrapolation is more realistic, but, both methods show clearly an increased B_{irr} for chemically treated wires A1–A4.

Resistive measurements of MgB_2/Fe wires do not allow to quantify the resistivities of MgB_2 cores sheathed (shunted) by Fe/Fe_2B [2] and consequently the Rowell analysis of grain-connectivity [10] cannot be applied. Therefore, MgB_2 cores were carefully extracted from the iron sheath, which allowed measuring their resistances versus temperature and estimating the correct value of ρ_{MgB2} [11]. Fig. 5a presents the normalized resistances of A0–A4 samples in the scale of temperature 35–41 K. Systematic improvement of the resistive transition with decreased acetic acid concentration (10 vol.% → 0.3 vol.%) is apparent. Critical temperatures estimated as a middle of the transition $T_{c\text{-}midd}$ and the width of transition ΔT_c are improving with decreased acetic acid concentration (see Table 2). The highest $T_{c\text{-}midd} = 39.7$ K and the narrowest transition $\Delta T_c = 0.4$ K was measured for A0 core, which confirm that all chemical treatments have lead to less purity MgB_2 phase.

The MgB_2 resistivities (ρ_{MgB2}) are shown in a wide scale of temperatures (25–300 K) by Fig. 5b. Nearly two orders of magnitude differences in ρ_{MgB2} are visible as a consequence of applied chemical treatments by acetic acid. No one of samples has lower resistivity than not treated sample A0. Room temperature resistivity ρ_{MgB2} of presented cores is ranging from 75 to 3000 µΩ cm, which is considerably higher than for MgB_2 films ~10 µΩ cm [12] and in situ bulk samples 20–50 µΩ cm [13]. The highest ρ_{MgB2} corresponds to sample A4 reflecting the lowest core purity. Similar $\rho_{MgB2}(T)$ dependences are measured for A1 and A0 due to the lowest acid concentration with properly applied purification process, (see Table 2). Although A1 and A0 have nearly the same