Journal of Alloys and Compounds 724 (2017) 507–514

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Solution-processed nanometers thick amorphous carbon-coated boron as an efficient precursor for high-field performance of MgB_2

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ARTICLE INFO

Article history:
Received 20 February 2017
Received in revised form
13 June 2017
Accepted 3 July 2017
Available online 4 July 2017

Keywords:
MgB_2
PMMA

ABSTRACT

We report the fabrication of high-performance MgB_2 bulk superconductors doped with amorphous carbon (aC), derived from PMMA polymer, a safe and cost effective carbon source as compared to explosive gaseous and expensive C-containing nanoadditives. The commonly used C-containing nanoadditives and boron (B) precursor nanopowders are usually prone to agglomeration in solid state mixing which causes poor reactivity and non-uniform distribution that leads to deterioration of critical current properties of MgB_2. We have overcome this problem by achieving uniform 3–4 nm thin coating of aC on B nanopowders by pyrolysis of PMMA through solution process. Compared to undoped MgB_2, significantly high current-carrying capability (J_c (5 K, 8 T) ~3.1 × 10^4 A/cm^2 and J_c (20 K, 6 T) > 10^3 A/cm^2) was obtained for aC-doped MgB_2, which is comparable to the record high in-field J_c reported for SiC-doped MgB_2 and much better than those reported in literature with other C sources. Furthermore, significant improvement in H_{irr} and H_{c2} were also observed for aC-doped MgB_2. The improved high-field properties in PMMA-derived aC-doped MgB_2 bulk suggest that the solution process could be a powerful technique to obtain uniform mixture of C-coated B to develop high-performance $Mg(B_{1-x}C_x)_2$ wires for practical applications.

1. Introduction

Doping of carbon (C) containing nanomaterials into MgB_2 has proven to be very effective in pinning the magnetic vortices and improving its superconducting performance at high fields [1], which is very important for practical applications [2]. The superconducting performance strongly depends on the distribution of nanodopant within the MgB_2 matrix. There has always been a problem of agglomerate formation of nanoadditives and starting precursor nanopowders in solid state mixing. Therefore, it was a great challenge for researchers to achieve homogeneous distribution of a nanodopant in MgB_2 through the dry mixing of powders. Zhou et al. proposed a wet mixing process to solve this problem by pre-mixing of carbohydrates, such as sugar ($C_6H_{12}O_6$) [3] and malic acid ($C_4H_6O_5$) [4] with boron powder in a solvent. However, carbohydrates introduce a large amount of oxygen (O) during sintering process, resulting in high content of MgO in MgB_2. In addition, the mixing of carbohydrates, mainly sugar increases the resistivity values by almost ~3 times as compared to that of the pure sample, which blocks the flow of supercurrent at self-field and low-field regions [5]. Recently, Ye et al. reported a new method to overcome this problem by achieving C-coating on boron (B) powder by incorporating an aromatic hydrocarbon, coronene ($C_{24}H_{12}$) as a carbon source [6]. However, despite many advantages of coronene, it faces a major drawback of being very expensive.

The C-coated B precursor powders have also been obtained by using gaseous sources of carbon. Kim et al. prepared C-encapsulated B powder by decomposing methane (CH_4) gas using radio frequency (RF) plasma technique, and obtained reasonably good critical current density (J_c) properties [7]. Recently, Liu et al. used commercially available C-coated amorphous B powders supplied by Pavezyum Advanced Chemicals, Turkey [8]. However, they did not

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http://dx.doi.org/10.1016/j.jallcom.2017.07.028
0925-8388/

succeed in obtaining plausible J_c results at high temperatures and high fields. In addition, the C coating on B powders was achieved from explosive hydrocarbon (C_xH_y) gases using complex RF plasma techniques. However, on the contrary, polymethyl methacrylate (PMMA) polymer turns out to be a non-toxic, safe to handle and cost effective solid carbon source [9]. PMMA is mostly used to convert its amorphous thin films into monolayer or few-layer graphene by heating at elevated temperatures ≥1000 °C [10]. Park et al. doped PMMA in MgB_2 wires through a wet mixing process and they have reported only some preliminary results [11]. In addition, the wet mixing process is undesirable because the dopants decompose near the formation temperature of MgB_2, as a result other byproducts such as O, H_2O, and CO etc. are released from the dopant, and these byproducts affect the superconducting properties adversely. Therefore, in the present work, we propose a different approach; PMMA was first decomposed at temperatures ≤800 °C to obtain a uniform coating of amorphous carbon (aC) on B powders through a solution process and then the aC-coated B powder was mixed well with appropriate amount of Mg. The mixed powders were pelletized and sintered at 700 °C for 30 min under Ar atmosphere.

The thin aC layer obtained this way on B precursor powders has the following benefits: (1) in contrast to oxygen containing carbon dopants, this layer is free of oxygen, thus it may help to reduce or maintain the same level of MgO impurity as in case of undoped sample. The insulating MgO is the main hindrance for the transfer of superconducting current between adjacent MgB_2 grains and results in a lower critical current [12]. (2) Since the binding energy of the amorphous phase is lower than that of the crystalline phase [13], the aC layer will have a lower melting temperature (T_M). Thus, we expect that the thin amorphous carbon layer can be decomposed easily during sintering process [14]. (3) Another advantage of the core-shell structure of C coated B is that the fast reaction rate between C and B could be expected. This is in contrast to dry mixing and wet mixing processes, where the reaction rate could be slowed down by the requirement of decomposition of C-containing compounds as well as the formation of secondary phases by the reactions between decomposed products and Mg, such as Mg_2Si [15], Mg_2C_3 [13] and MgO etc. (4) The superconducting parameters, such as critical temperature (T_c), critical current density (J_c) and upper critical field (H_{c2}) of MgB_2 are very sensitive to the amount of C substitution for B [1]. Usually, high level of C doping enhances J_c at high fields but decreases J_c at low fields and also causes significant reduction in T_c. In the aC-coated B precursor powder proposed in this work, the amount of C substitution could be easily controlled by simply controlling the thickness of the aC layer which depends on the weight percent of PMMA in solvent [16]. Thus, in contrast to other methods [3,6–8], solution process could pave a better way to control the amount of C substitution for B which is very important for fabricating long length MgB_2 wires for practical applications.

2. Experimental details

Fabrication of amorphous carbon-doped MgB_2 was carried out in two steps:

2.1. Coating of amorphous carbon on B nanopowders

A solid carbon source, PMMA $(C_5O_2H_8)_n$ powder from Sigma Aldrich with 5 wt. % of total MgB_2 was dissolved in a solution of N,N-dimethyl formamide (DMF). DMF was used as a solvent. Then, boron nanopowders (average size < 100 nm from Specialty Materials Inc., USA) were thoroughly homogenized in as-prepared PMMA solution. The boron/PMMA composite was drop-cast on Si wafer and then left for drying followed by pyrolysis process at different temperatures of 500 and 800 °C under Ar atmosphere for 3 h, respectively. The pyrolysis at two different temperatures was done to check the reproducibility of the samples as well as to study the effect of amorphous carbon on superconducting properties of MgB_2. The aC coating on B powders was anticipated by decomposition of PMMA, since the thermal decomposition temperature of PMMA is ~310 °C [17]. Fig. 1 schematically illustrates the coating process of PMMA-derived amorphous carbon on the surface of B nanopowder. The pyrolysis process can be described by the following chemical reaction equation,

$$(C_5O_2H_8)n + xB \rightarrow x(B{-}C) + yH_2O\uparrow + zH_2\uparrow + CO\uparrow \quad (1)$$

2.2. Synthesis of amorphous carbon-doped MgB_2

For the synthesis of PMMA-derived aC-doped MgB_2 samples, appropriate amount of Mg (<2 μm from Tangshan Weihao, China) was milled with aC-coated B precursor powders prepared at different pyrolysis temperatures. The mixed powders were transferred into a mold of 10 mm × 10 mm in size to form a pellet under 10 Ton pressure using uniaxial hydraulic press. A reference pellet sample of undoped MgB_2 was also prepared for comparison. The pellets were put into Fe tubes and sintered *in situ* at a temperature of 700 °C for 30 min under the flow of high-purity Ar gas (5N). Finally, the undoped and doped samples were cooled down to room temperature in a continuous flow of Ar gas. The MgB_2 samples doped with amorphous carbon which was derived from PMMA at different pyrolysis temperatures are referred to as a C_pyrolysis temperature-doped MgB_2 in the text.

2.2.1. Characterizations

Raman spectroscopy was used to observe the carbonization of PMMA polymer. The high-resolution transmission electron microscopy (HRTEM) analysis was performed to confirm the coating of amorphous C on the surface of B nanopowders. The crystal structure of aC-doped and undoped MgB_2 samples were investigated by X-ray diffraction (Rigaku, D/Max 2500) using Cu Kα as an X-ray source. The microstructures of samples were examined by field emission scanning electron microscopy (FESEM). The magnetization measurements, magnetization versus temperature (*M-T*) and magnetization hysteresis (*M-H*) loops were carried out on all samples by using a quantum design vibrating sample magnetometer option (PPMS, Quantum Design). The magnetic field varying from −9 T to +9 T was applied parallel to the longest dimension of the samples. The J_c was estimated from $M{-}H$ loops by Bean's critical state model, $J_c = 20\Delta M/a(1\text{-}a/3b)$, where ΔM is the height of the $M{-}H$ loop, a and b are the thickness and width of the sample, respectively. The upper critical field (H_{c2}) and irreversibility field (H_{irr}) were estimated from resistivity measurements which were performed under an applied field of 0–8 T using a quantum design AC transport measurement option (PPMS, Quantum Design).

3. Results and discussion

The formation of amorphous carbon on the boron nanopowders was verified by Raman spectroscopy. The Raman spectrum of aC-coated B precursor powders after pyrolysis of PMMA at 500 °C is shown in Fig. 2a. The peaks around 1350 (D band) and 1580 cm^{-1} (G band) are typical for amorphous carbon [18]. This result indicates that after pyrolysis process PMMA was converted into amorphous C. The amorphous nature and uniformity of C on B were also confirmed with high-resolution transmission electron microscopy (HRTEM) investigation. In the TEM image, Fig. 2b, clear lattice