Materials Chemistry and Physics 138 (2013) 192–198

Contents lists available at SciVerse ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Analysis of the precipitation process of secondary phase $MgNi_{2.5}B_2$ and superconducting properties in Ni-doped MgB_2 bulk

Qian Zhao, Yongchang Liu*, Qi Cai

Tianjin Key Lab of Composite and Functional Materials, School of Materials Science & Engineering, Tianjin University, Tianjin 300072, PR China

HIGHLIGHTS

- The morphology of $MgNi_{2.5}B_2$ was related with the Ni particle sizes.
- The coarse Ni produced $MgNi_{2.5}B_2$ clusters with large size at the grain boundaries.
- The concentration of clusters acted as weak links and reduced the intergrain J_c.
- The fine Ni promoted the formation of refined $MgNi_{2.5}B_2$ particles inside MgB_2 grains.
- The precipitation of tiny $MgNi_{2.5}B_2$ particles had less effect on J_c.

ARTICLE INFO

Article history:
Received 24 October 2011
Received in revised form
19 October 2012
Accepted 25 November 2012

Keywords:
Superconductors
Sintering
Differential thermal analysis (DTA)
Superconductivity

ABSTRACT

A polycrystalline MgB_2 sample with 4 at.% Ni powder addition has been synthesized by a solid-state reaction at 750 °C. Two different Ni powders, raw (40 μm) and ball-milled (10 μm) particles were selected to clarify the influence of the Ni particle size on the secondary phase $MgNi_{2.5}B_2$ formation and the critical current density J_c of MgB_2 bulks. According to the investigation of the sintering, it was found that the smaller Ni particles may significantly decrease the formation temperature of the $MgNi_{2.5}B_2$ ternary compound to 550 °C. Combined with scanning electron microscopy (SEM) analysis and magnetic measurements, it was suggested that the addition of fine Ni particles led to $MgNi_{2.5}B_2$ inclusion precipitating along the spiral terraces of MgB_2 grains and with small particles sizes. The unique microstructure is responsible for the smaller reduction in J_c, which partly eliminates the effect of weak links compared with the coarse Ni particles. Besides, the formation mechanism of the microstructures and the relative location of $MgNi_{2.5}B_2$ varying from cluster at the MgB_2 grain boundaries to a screw arrangement around the MgB_2 grains with the decrease of the Ni grain sizes were also discussed in detail.

1. Introduction

Since the discovery of the superconductivity in the simple binary intermetallic superconductor magnesium diboride (MgB_2), it has attracted much attention for decades in both fundamental properties and practical applications [1]. Compared to high-temperature superconductors (HTS), MgB_2 has a simple structure, low anisotropy and weak link free grain boundaries [2]. However, the rapid degradation of critical current density (J_c) with the applied magnetic field is still a serious problem to be overcome [3,4]. The studies during the past few years show a significant improvement of critical current density in MgB_2 by elemental substitutions and addition of compounds. Among these dopants, nano-SiC doping has resulted in a record high in-field J_c–H in MgB_2, the disorder on the lattice sites by partial substitution of C for B and the highly-dispersed nano-inclusions within the grains as effective pinning centers are the main reasons for improving the J_c behavior [5–7]. Simultaneously, plenty of experimental work is focused on finding the appropriate elements for the substitutions on Mg sites, such as metal elements (Ti, Fe, Al, Ni, Li, Cu, Mn and Ag) [8–15]. Unfortunately, only a few metal elements (Al, Cu and Li) [16–20] were proven to be real substitutes onto Mg sites. In particular, Al substitution has been studies by a number of groups since AlB_2 has the same crystal structure to MgB_2. However, the results show that the critical temperature (T_c) of MgB_2 undergoes a dramatic decrease and even the loss of superconductivity with the Al content increases [18].

Most of the metal elements are found to react with either Mg or B forming intermetallics (FeB, Mg_2Cu, MgAg, $MgZn_2$ among others) instead of substitution, if the impurity particles are at nano-scale,

* Corresponding author. Tel./fax: +86 22 87401873.
E-mail address: licmtju@163.com (Y. Liu).

0254-0584/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matchemphys.2012.11.043

the J_c value would be eventually enhanced by inducing more flux pinning centers in MgB_2. Kumar et al. [21] announced that the presence of $AgMg_3$ in the form of small 10–20 nm precipitates in a Ag-doped MgB_2 sample resulted in high critical currents in magnetic fields. Similarly, the LaB_6 and TiB_2 nanoparticles inclusions in the MgB_2 matrix also increased J_c by doping of La and Ti [22,23]. In contrast, several metal elements including Zn, Cu, Na and Ca are all proven to be negative effects on the superconducting properties of bulk MgB_2 because of the large size of the impurity grains (>1 μm) [24]. Hence, metallic nano-particle doping has aroused considerable interest in expect of successfully inducing nanoparticle in the MgB_2 matrix. Varghese et al. reported the enhanced transport J_c values at low synthesis temperatures (550 °C) by a small amount of nano-Cu addition [25]. Moreover, the fine particle inclusions inside MgB_2 grains are found to be responsible for the intra-grain flux pinning [26] in the samples doped with nano-sized Si (less than 100 nm). But not all the doped nanoparticles are positive candidates for enhancing the J_c and even some of them may negatively affect the J_c in in-field performance, such as nano-Fe doping. Dou et al. found that the $J_c(H)$ was severely decreased in nanoscale Fe particle doped samples, which confirmed that the FeB and FeB_2 particles formed not inside MgB_2 grains but at grain boundaries may lead to weak links and thus to the reduction in zero-field J_c [27].

Therefore, it can be concluded that the effect of metal elements doping on the superconducting properties is not only related to the particle size but also strongly depends on the location of the secondary phase in MgB_2 matrix. The inclusions locating inside the MgB_2 grains with small grain size are believed to act as effective pinning center and increase the critical current density in magnetic field. On the contrary, the concentration of the inclusions at MgB_2 grain boundaries can deteriorate the connectivity between MgB_2 grains and thus decrease the J_c values. As a result, it is of crucial importance to clarify relative location between the MgB_2 grains and the secondary phase in the samples with different particle size doping. In our previous works, the trend of Ni particles sizes-dependent superconductivity has been traced, but the intrinsic mechanism is not clear for characterizing these changes [28]. In this study, two different Ni powders, raw (40 μm) and ball-milled (10 μm) particles were used as dopant in MgB_2 matrix. Combined with DTA analysis and in situ XRD experiments, the relationships between the Ni particle size and the formation temperature of the inclusions are well demonstrated. Moreover, according to the investigation of the sintering and unique microstructure, the relative location of the inclusion is found to strongly rely on the Ni grain size, subsequently influencing the superconducting behavior of MgB_2 in high magnetic field.

2. Experimental details

The Ni-doped MgB_2 pellets were prepared by an in situ reaction process with different Ni powders. The ball-milled Ni powders were obtained using raw powder in a planetary ball mill with agate balls under the protection of Ar atmosphere for 10 h. The morphology and particle size of the powders are exhibited in Fig. 1. As for the raw Ni powder, the spherical particles size is about 40 μm. In contrast, as seen in Fig. 1(b), the milled-Ni particles exhibit lamellar outlines and are further decreased the size to about 10 μm.

After the milling, Mg powder (99.5% purity, ~100 μm) and amorphous boron powder (99% purity, ~25 μm) were mixed with Ni powders with different particle sizes (40 μm and 10 μm) in the molar ratio of $(MgB_2)_{0.96}Ni_{0.04}$. The mixture was thoroughly grinded in an agate mortar, and then mechanically pressed into cylindrical pellets ($\Phi 5 \times 1.5$ mm^2) under a pressure of 5 MPa. In order to obtain thermokinetic information during the sintering, all samples were also heat-treated and analyzed simultaneously using Differential Thermal Analysis (DTA) at 750 °C for 30 min with a heating rate of 5 K min^{-1} under high purity Ar flow.

The phase composition of the pellets was detected using in situ X-ray diffractometer (XRD). The microstructural characteristics were investigated by SEM (XL30ESEM). The magnetization of the bulk samples was measured by a MPMS-5 superconducting quantum interference device (SQUID) magnetometer. The critical temperature (T_c) was obtained from the temperature dependence of the normalized zero field cooled (ZFC) magnetization. The magnetic J_c was calculated from the height of magnetization hysteresis loops based on the Bean model$J_c = 20\Delta M/[a/(1 - a/3b)]$. In order to compare the magnetic properties of different samples, all of them are cut into rectangles ($1.0 \times 2.1 \times 4.2$ mm^3).

3. Results and discussion

In order to well understand the transformation process upon the changes of Ni grain sizes, the Ni-doped MgB_2 samples were studied by thermal analysis. The recorded DTA curves are illustrated in Fig. 2. Normally, as for the pure MgB_2 bulk, DTA curves contain three thermal peaks, which correspond to solid–solid reaction, solid–liquid reaction, and Mg melting. The similar procedure can also be found in the curves of the Ni-doped sample, which is marked as peak 1, peak 2 and peak 3. However, an extra exothermic peak labeled by Peak 4 appeared for the 40 μm Ni-doped sample. Interestingly, this peak also disappeared for the 10 μm Ni-doped sample. It is reported that the samples with Ni addition show significant reaction and resulted in the formation of large quantities

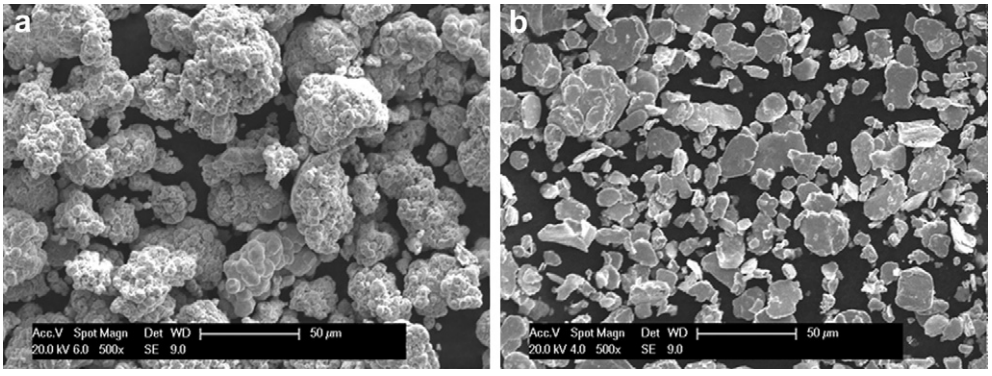

Fig. 1. The SEM images of (a) the raw and (b) the ball-milled Ni powders.