Physica C 470 (2010) 648–653

Contents lists available at ScienceDirect

Physica C

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

Effect of processing variables on the reaction kinetics of MgB_2 fibers

John D. DeFouw *, David C. Dunand

Department of Materials Science & Engineering, Northwestern University, Evanston, IL 60208, USA

ARTICLE INFO

Article history:
Received 1 April 2010
Accepted 7 June 2010
Available online 10 June 2010

Keywords:
Reaction kinetics
X-ray diffraction
Magnesium diboride
Thermal cycling

ABSTRACT

The reaction kinetics for converting B fibers into MgB_2 fibers are measured by *in situ* synchrotron X-ray diffraction and *ex situ* by metallography as a function of the following processing variables: fiber diameter, fiber doping, fiber surface treatment, Mg flux (liquid or gaseous Mg), and thermal cycling. Changes to the fiber diameter, surface treatment and Mg flux affect little the rates of the reaction, while C-doping of fibers dramatically decreases reaction rate and thermal cycling increases the reaction rate.

1. Introduction

The boride MgB_2 is a promising new superconducting material due to its combination of relatively high transition temperature (T_c = 39 K), lack of weak link behavior at grain boundaries, low cost of elements, and ease of synthesis from the elements [1]. The reaction kinetics for synthesis of MgB_2 from elemental Mg and B:

$$Mg + 2B = MgB_2 \quad (1)$$

have been studied between Mg vapor and a B thin film [2] and between Mg and B powders [3–6], and take place via the creation of intermediate borides (mainly MgB_4 and very little MgB_7). The reaction is described as a diffusional process with temperature as the primary parameter to alter the reaction kinetics. By measuring reaction rates as a function of temperature and modeling the geometry of the powders or film, the reaction kinetic parameters (i.e., diffusion coefficients, rate constants, and activation energies) were determined [2,3]. Recently, the analysis was extended to reacting B fibers and liquid Mg to MgB_2 fibers [7] where the large diameter of the B fibers (140 μm) and extensive reaction volume expansion (90% volume increase from B to MgB_2) induced cracking during synthesis, which increased the surface area and thus accelerated the diffusion controlled MgB_2 synthesis reaction [7]. In that study, the only processing variable studied was temperature.

In the present paper, we study additional processing parameters affecting the reaction of B fibers into MgB_2: B fiber size (100 vs. 140 μm), Mg flux (Mg vapor vs. Mg liquid), surface of the B fibers (with and without a thin nitride layer), chemistry of B fibers (with and without doping with 0.4 at.% C), temperature profile (isothermal vs. thermal cycling) and fiber length (continuous vs. fragmented). This systematic study allows the identification of the parameters affecting the MgB_2 synthesis kinetics.

2. Material and methods

The reaction of B fibers immersed within liquid Mg was studied *in situ* by synchrotron diffraction, as described elsewhere [3,7]. In brief, bundles of 20 mm long B fibers were first pressure infiltrated with liquid Mg inside a titanium crucible. The sample was later heated under Ar cover gas to the reaction temperature in a custom furnace, while a high energy X-ray beam passed through the sample and produced a diffraction pattern on a CCD camera. Through measuring diffraction intensity with time, the kinetics of the reaction were determined. Here, several experiments were conducted to investigate the effects of various parameters on reaction rates and MgB_2 microstructure. First, 100 μm diameter B fibers (from Specialty Materials, Inc., Lowell, MA) were reacted in liquid Mg at 900–1000 °C and compared to data on 140 μm diameter B fibers (from Specialty Materials, Inc., Lowell, MA) collected in previous research [7]. Second, the above 100 μm B fibers were also reacted at 900–1000 °C with Mg vapor, with a flux related to the vapor pressure of Mg reduced as compared to experiments with liquid Mg carried out at the same temperatures. Third, fibers of 140 μm diameter (from AVCO, with similar W fiber core) with a thin 1–2 μm outer nitride coating created by first oxidizing the fiber then reacting with ammonia [8] were reacted in liquid Mg at 900–1000 °C and compared with previous data on uncoated 140 μm B fibers [7]. In a fourth series of experiments, 85 μm diameter B fibers doped with 0.4 at.% C – synthesized by Specialty Materials, Inc. through decomposition of CH_4 and BCl_3 during the chemical vapor deposition (CVD) on a W fiber [9] – were studied *ex situ* by

* Corresponding author.
E-mail address: jdefouw@u.northwestern.edu (J.D. DeFouw).

0921-4534/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.physc.2010.06.007

metallography after reaction at 1000 °C for 5 min and 2.5 h in liquid Mg to investigate the effect of C upon reaction rate.

The low surface to volume ratio of continuous B fibers with >100 μm diameter slows their reaction rate as compared to the much finer B powders studied to date [3]. One possible path to improve reaction rate of fibers is to enhance, during the reaction, cracking of the boride layer growing radially into the B fiber by exploiting the differences in thermal expansion between the unreacted boron and the growing boride layer. To this end, reaction rates between liquid Mg and 140 μm B fibers were measured under thermal cycling conditions, and compared to baseline isothermal conditions. The temperature was cycled across 668–900 °C (ΔT = 232 °C) and 737–900 °C (ΔT = 163 °C) while isothermal baseline experiments were conducted at the upper temperature of 900 °C. The cycles were approximately square with near linear cooling to the lower temperature in 1 min followed immediately by heating back to 900 °C in 1 min where it was then held for 28 min (30 min period, 10 cycles) or 8 min (10 min period, 30 cycles) resulting in 5 h total reaction time. Finally, to investigate the geometrical effect associated to the continuous nature of the fibers, 100 μm B fibers were mechanically fractured into 25–45 μm fragments which were reacted with liquid Mg at 900 °C and compared to continuous fiber reactions at the same temperature. Also, for comparison, large (60–140 μm) irregular crystalline B powders (form Alfa Aesar, Ward Hill, MA) were reacted at 800 °C for 2 h in liquid Mg and imaged using optical microscopy.

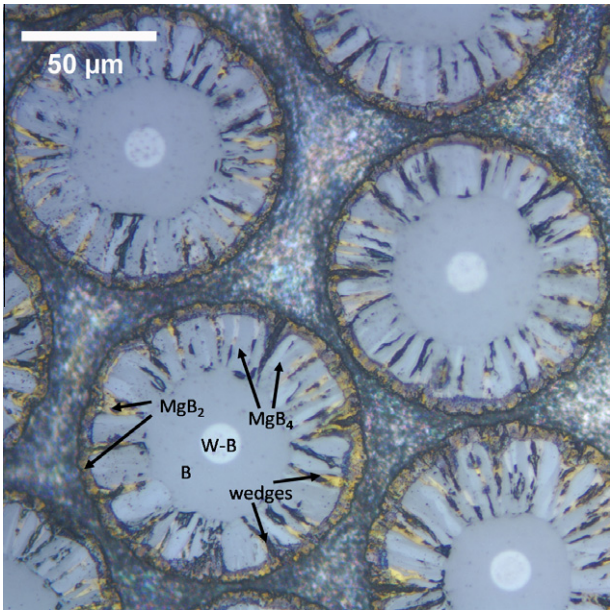

Fig. 2. Optical micrograph showing cross-sections of 100 μm B fibers reacted for 3 min at 1000 °C.

3. Results and discussion

3.1. Fiber diameter

Fig. 1 shows reaction kinetic plots for 100 μm diameter B fibers, where the degree of reaction is plotted as a function of reaction time. The reaction rate decreases monotonically with time, and reaction is completed in ~1 h at 1000 °C, ~2 h at 950 °C and ~4.5 h at 900 °C. Times to achieve full reaction were similar to those previously measured on 140 μm diameter fibers, despite the higher volume (by a factor two) of the latter fibers. By contrast, the Entchev diffusion model presented in Refs. [3,7,10], which assumes a reaction front progressing radially in the B fiber without cracking, predicts that a 100 μm diameter B fiber reacts to MgB_2 in 51% of the time needed for a 140 μm B fiber to fully react. This model predicts much longer reaction times than experimentally observed here, because it does not take into account the cracking of the reaction layer, observed in previous experiments with 140 μm B fiber [7] and in the present experiments (Fig. 2), which increases the area of the fiber available for reaction and thus decreases reaction times.

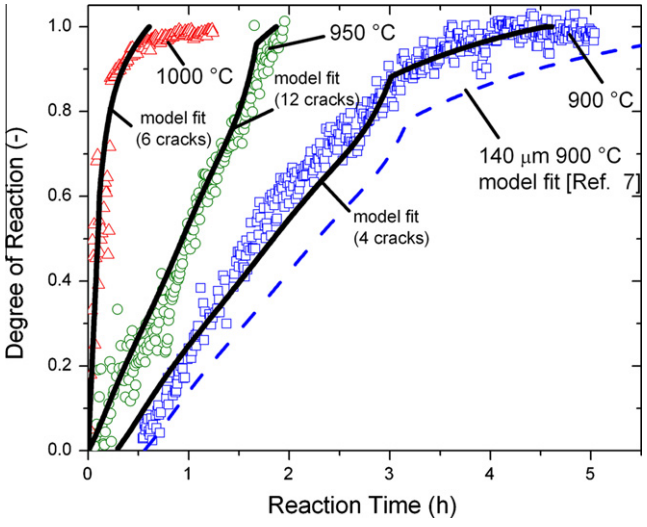

Fig. 1. Degree of reaction vs. time plot for 100 μm B fibers reacted in liquid Mg between 900 and 1000 °C with diffusion and cracking model fits using diffusion coefficients within the uncertainty measured in previous research [7]. A dashed line of the fit of the reaction of larger 140 μm diameter fibers [7] is shown for comparison.

A more complex model taking into account reaction layer cracking [7] also predicts complete reaction of the smaller 100 μm diameter B fiber in about half the time of the larger 140 μm B fiber, assuming that the fibers contain four cracks and choosing diffusion coefficients which fit the curves shown in Fig. 1. In this figure, fits of this cracking model to reaction kinetics data of 100 μm B fibers at 900 °C are best achieved with the following parameters: number of cracks: $N = 4$; MgB_2 diffusion coefficient: $D_{MgB2} = 6 \times 10^{-14}$ m^2 s^{-1}; MgB_4 diffusion coefficient: $D_{MgB4} = 5 \times 10^{-13}$ m^2 s^{-1}; and a shift of 18 min to account for some incubation time. Similarly, 1000 °C data for reaction of 100 μm B fibers are best fit with $N = 6$, $D_{MgB2} = 1 \times 10^{-12}$ m^2 s^{-1}, and $D_{MgB4} = 12 \times 10^{-12}$ m^2 s^{-1}. Finally, the 950 °C reaction curve of 100 μm fibers is best fit by $N = 12$, $D_{MgB2} = 8 \times 10^{-14}$ m^2 s^{-1}, and $D_{MgB4} = 8 \times 10^{-13}$ m^2 s^{-1}. All three fits are plotted in Fig. 1 and the parameters for the fits are close those found in a previous study for 140 μm diameter fibers [7]. A relatively high number of cracks is needed to fit the very linear nature of the experimental reaction curve. As discussed in Ref. [7], the curves typically have a transition from a fast to a slower reaction rate which corresponds to the point where MgB_2 wedges growing radially in the fiber meet its center and radial circumferential diffusion becomes the sole active mechanism. With a high number of cracks, the curves become more linear since more of the fiber is reacted by the radial crack mechanism, resulting in less material being reacted by the slower diffusion mechanism.

The microstructure of the 100 μm diameter fibers reacted at 1000 °C for 3 min is shown in Fig. 2 and is similar to that found for 140 μm diameter fibers [7]. The reaction layer consists of an outer ring of MgB_2 and an intermediate layer of MgB_4 and the extents of the reaction fronts (4 and 22 μm, respectively) are similar to those reported previously for 140 μm fibers [7]. In both cases,