Synthesis of nanoscale magnesium diboride powder

D K Finnemore\(^1\) and J V Marzik\(^2\)

\(^1\) Ames Laboratory USDOE and Iowa State University, Ames, Iowa, US
\(^2\) Specialty Materials, Inc., Lowell Massachusetts, USA

E-mail: finnemor@ameslab.gov

Abstract. A procedure has been developed for the preparation of small grained magnesium diboride (MgB\(_2\)) powder by reacting nanometer size boron powder in a magnesium vapor. Plasma synthesized boron powder that had particle sizes ranging from 20 to 300 nm was mixed with millimeter size chunks of Mg by rolling stoichiometric amounts of the powders in a sealed cylindrical container under nitrogen gas. This mixture then was placed in a niobium reaction vessel, evacuated, and sealed by e-beam welding. The vessel was typically heated to approximately 830 °C for several hours. The resulting MgB\(_2\) particles have a grain size in the 200 nm to 800 nm range. Agglomerates of loosely bound particles could be broken up by light grinding in a mortar and pestle. At 830 °C, many particles are composed of several grains grown together so that the average particle size is about twice the average grain size. Experiments were conducted primarily with undoped boron powder, but carbon-doped boron powder showed very similar results.

1. Introduction

In this work, we report the development of a batch process for the conversion of plasma synthesized boron powder\(^1\) into MgB\(_2\) powder. Early studies of the performance characteristics of MgB\(_2\) conductors showed that the critical current density, J\(_c\), of a MgB\(_2\) wire was controlled primarily by grain-boundary pinning\(^2,3\). Hence, for an ex-situ powder-in-tube (PIT) process to fabricate MgB\(_2\) conductors, it is generally preferred to have small grain size for the starting MgB\(_2\) powder in order to give a dense array of grain boundaries in the final wire.

2. Experimental

In the procedures reported here to convert plasma synthesized boron powder into MgB\(_2\) powder, the boron powder and the magnesium were handled in a glove box under dry nitrogen. Samples were transported in sealed glass jars filled with N\(_2\). The plasma synthesized boron powder was mixed with millimeter size chips of Mg by rolling stoichiometric amounts of the elements in a Mason jar under dry N\(_2\) gas for about 10 minutes. This mixture was then placed in a cylindrical Nb reaction vessel (28 mm OD x 150 mm long x 1 mm wall thickness). An end cap was affixed and the tube was evacuated prior to closing the tube by e-beam welding. The vessel was heated to 830 °C for 24 h in a horizontal furnace under an argon atmosphere. A tubing cutter was used to open the reaction vessel near the weld, and the powder was poured into a Mason jar for storage in the glove box. The powder tended to form agglomerates up to a centimeter in size but these could be broken up by light grinding in a mortar and pestle.

As shown in figure 1, most of the grains are in the 100 to 800 nm range for a sample reacted at 830 °C for 24 h. A sputter coating of iridium (~2 nm) was applied to highlight the shape and size of the particles for examination in the scanning electron microscope (SEM). At the reaction temperature some grains grew together to make elongated particles (figure 1). Figure 2 illustrates a particularly large particle where the grains linked up into a particle ~2000 nm long.
Figure 1. Scanning-electron Microscope micrograph illustrating the grain size and connectivity for MgB$_2$ reacted at 830°C for 24 h.

Figure 2 A micrograph showing a particularly large particle where several grains have grown together for powder reacted at 830°C for 24 h.

A rough estimate of the distribution of both the particle size and the grain size distribution was made by taking many of micrographs at 15,000x and 50,000x and taking the long dimension on the micrograph as a measure of the particle size. Typically the largest 124 of the particles were used in the viewing fields of four micrographs, so these measurements ignored the smallest grains and particles. The results are shown in figures 3a & 3b. Measurements of the average grain size have a lot of uncertainty but the average grain size seems to diminish from about 600 nm for a 48 h reaction at 830°C to about 300 nm for an 8 h reaction at 830°C.

We also prepared three 50g batches of Mg[B$_{0.98}$ C$_{0.02}$]$_2$. Carbon was added by introducing CH$_4$ to the gas stream in the plasma synthesis of the boron powder. The results were indistinguishable from the work shown above for the undoped boron.

Figure 3. (a) Grain size and (b) particle size and distribution estimated from 3 different 50 g batches of MgB$_2$ powder as measured for 124 grains or particles from each batch. The grain or particle size average length is labeled for the bin being counted. Note 1 particle is shown at 2906 nm in (b).
If the reaction temperature was raised and the reaction time extended, the particles got larger and more interconnected as illustrated by the micrograph in figure 4 for a sample reacted at 860°C for 48 h.

*Figure 4.* SEM micrograph of MgB$_2$ powder reacted at 860°C for 48 h.

*Figure 5.* Micrograph of MgB$_2$ particles grown at 830°C for 8 h.

If the reaction time at 830°C was reduced to 8h, the average particle size was distinctly smaller as shown in figure 5.

Figure 6 shows a quantitative measure of the average grain size for different reaction times at 830°C. Four micrographs were taken at 50,000x, the largest linear dimension of each grain was used as a measure of the grain size, and the average of 124 of the largest particles was used for each reaction time.

*Figure 6.* Plot showing the average grain size as a function of reaction time.

As the reaction time was reduced, there was an increasing chance that some higher borides such as MgB$_4$ or some MgB$_7$ formed in the resulting powder, indicative of an incomplete reaction between Mg and B. For the shortest time reported here of 8 h at 830°C, we do not see any regions of MgB$_4$ or MgB$_7$ in the SEM nor in the X-ray diffraction pattern of the powder in figure 7 below. If there
were diffraction lines from MgB$_{4}$ or MgB$_{7}$, they were below the level of detection indicating that they must be at least less than a couple of percent.

Figure 7. X-ray diffraction pattern for MgB$_{2}$ powder for a reacted at 830°C for 8 h using Cu-K$_{a}$ radiation. All the lines above the noise are MgB$_{2}$ except two, one marked as a probable MgO line and one not identified as indicated.

In carrying out this study, we attempted several variants on the above procedure, each of which had some shortcomings. In our early exploration of this problem, we had hoped to use an iron reaction vessel because the cost is relatively low compared to the likely alternatives of niobium or tantalum. We found, however, that the superconducting transition temperature of the MgB$_{2}$ powder that was synthesized in an Fe vessel consistently had a transition temperature, T$_{c}$, of about 2 K lower than the T$_{c}$ of similar powder prepared in a Ta or Nb reaction vessel (figure 8).

Figure 8. Comparison of T$_{c}$ for MgB$_{2}$ powder grown in Fe or Ta reaction vessels

Figure 9. MgB$_{2}$ particles from reaction in an Armco Fe reaction vessel held at 970°C for 18 h.

In addition, the Fe also seemed to promote the growth of large hexagonal grains of MgB$_{2}$ as shown in figure 9. Often grains as large as 5 micrometers were found and the particles tended to form as platelets rather than equiaxed particles. The vapor pressure of Fe at 1000°C is $10^{-6}$ torr but that
seemed to suffice to alter the grain growth. With these hints of difficulty, the reaction vessel material was changed to Nb and no further work was done with Fe.

Hence, for most of the work reported here, the experiments were done in cylindrical Nb reaction vessels. The typical batch size was approximately 50 grams. In a second variant to the process, the Nb cans were arc-welded shut in an argon atmosphere of half to three quarters of an atmosphere instead of e-beam welding in a vacuum. We found however, that the presence of argon slowed the diffusion of Mg vapor through the boron packed powders and made the conversion of the plasma synthesized boron powder to MgB$_2$ rather slow and erratic. The reaction rates seemed to depend on the details of the packing of the mix of Mg and B powder. When the Nb cans were e-beam welded shut in a vacuum, the rate and the completeness of the reaction seemed much less dependent on the quality of the packing of the reactants and the resulting grain size of the MgB$_2$ varied systematically with time and temperature. When the Ar was removed by using e-beam welding of the Nb vessel in a vacuum, the process of conversion of plasma synthesized boron to MgB$_2$ became quite regular.

3. Conclusions
Plasma synthesized boron powder with particle size in the 20 nm to 300 nm range, can be transformed into MgB$_2$ powder with particle size in the 100 nm to 1000 nm range by reacting the boron powder with magnesium vapor in an evacuated niobium reaction vessel at 830°C for about 24 h. Two alternate procedures gave unsatisfactory results. First, our attempts to use iron reaction vessels gave a systematically lower $T_c$ and resulted in a more plate-like growth habit than powders grown in Nb. Second, our attempts to seal the reaction vessel under argon by arc welding resulted in erratic and slow growth rates for the MgB$_2$. Conversion rates to MgB$_2$ were faster and more regular if the Nb vessel was sealed under vacuum with e-beam welding. The presence of argon in the reaction vessel slowed the diffusion of magnesium vapor through the boron packed powders and slowed the reaction of magnesium with the boron powder.

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5. References
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