

PLASMA SYNTHESIZED BORON NANO-SIZED POWDER FOR MgB₂ WIRES

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ABSTRACT

Plasma synthesized boron powder has been prepared under a variety of RF plasma conditions to examine the suitability of these powders for the preparation of powder-in-tube MgB₂ wire. Particle size emerging from the RF torch typically ranges from 5 nm to 200 nm and lattice imaging studies in a transmission electron microscope show large portions of both amorphous and beta rhombohedral crystalline material. *In situ* powder-in-tube wire that is made with a continuous tube filling and forming process consistently gives critical current densities ranging from 20,000 to 100,000 A/cm² at 5 K and 5 Tesla for a powder containing about 4% carbon. As the temperature rises, the critical current density of 100,000 A/cm² occurs at 4.3 T at 10 K, 3.5 T at 15 K, and 2.5 T at 20 K. In preparation for studies of an *ex-situ* powder-in-tube process, we have studied the size of reacted MgB₂ powder formed in a magnesium vapor. Reaction rates are much slower than for solid state diffusion in the *in-situ* process and care is needed to hold particle size under the micrometer range.

KEY WORDS: Superconductors, Nano-scale, Powders

INTRODUCTION

In recent years, there has been increasing interest in the synthesis of nano-sized metal and ceramic powders using RF, DC, and microwave plasmas [1], and the influence of nanoscale materials on a variety of ceramic, composite, and electronic materials. Previous work has shown that high performance superconducting MgB₂ wire can be made from plasma synthesized boron powder [2]. To raise the upper critical field, H_{c2}, and improve the performance of the critical current density, J_c, at fields above 5 T, carbon is doped into the boron by adding methane to the boron trichloride, BCl₃, and hydrogen, H₂, gas entering the plasma. Approximately 4% carbon will raise H_{c2} to above 30 T and substantially improves J_c at magnetic fields above 4 T. Transmission electron microscope studies have shown that the boron emerges from the plasma torch as very open and loose lacy agglomerates in which the size of the boron particles ranges from 5 to 200 nm [3]. A selected area diffraction scan shows prominent halos from the amorphous material and there are diffraction spots from the crystalline material (see Figure 1). Semi-quantitative

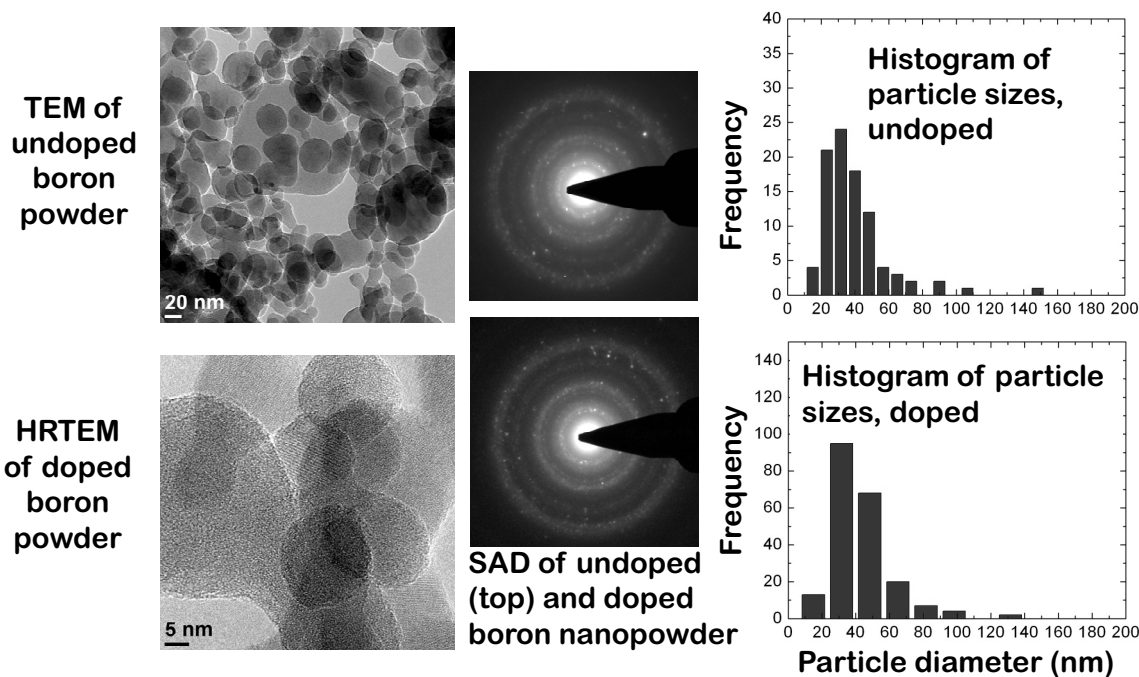


FIGURE 1. The plasma process for boron powder results in nano-sized particles with a mixture of amorphous and crystalline phases [3].

X-ray studies of changes in the background and peak areas indicate that there is somewhat more amorphous material than crystalline but there are substantial quantities of both [3]. These *in-situ* formed powder-in-tube (PIT) wires are usually reacted at 675 or 700°C to give a very fine grained MgB_2 core in which grain boundary pinning appears to be the dominant pinning force for the vortex lattice. The purpose of the work reported here is to study the temperature and magnetic field dependence of J_c in more detail and to compare J_c values for these powders with other high performance powders, specifically boron powder made from diborane, B_2H_6 . In addition, we begin to explore methods to prepare extremely fine grained MgB_2 powder for an *ex-situ* process.

EXPERIMENTAL

In the synthesis of boron powder, BCl_3 , H_2 , and dopant gas, typically CH_4 , were injected into an argon or argon/hydrogen RF plasma at reduced pressure [3]. The RF torch was powered by a Lepel T-30 power supply. The resulting boron powder was collected from the exhaust stream using sintered stainless steel filters in sealed housings. The powder was removed from the filter housings in a nitrogen glove box to avoid exposure to air.

A powder-in-tube (PIT) method was used for the fabrication of MgB_2 wire. The boron powder was mixed with Mg powder, and the combined powders were formed into wire in a continuous tube filling and forming (CTFF) process [2]. Typically, a niobium sheet was shaped into a channel into which the mixed Mg and B powder were placed. This channel was then closed into an overlapping Nb barrier. The powder filled tube was then inserted into a seamless $\text{Cu}_{0.7}\text{Ni}_{0.3}$ tube and drawn to final size. To make multi-filament wire, several monofilament tubes were stacked in a $\text{Cu}_{0.7}\text{Ni}_{0.3}$ can and the entire assembly was drawn to final size. The wires were subsequently heat treated at 650-700°C to fully

react the Mg and B. Critical current densities were measured by hysteresis [2] and transport methods [4] as previously reported.

RESULTS AND DISCUSSION

Analysis of MgB_2 wires made from nano-sized boron powder

Studies of the changes in $J_c(H, T)$ are illustrated in Figure 2 for two batches of undoped boron powder, one from the plasma synthesis process described herein and the other from the decomposition of diborane. The magnetic field at which J_c values cross $100,000 \text{ A/cm}^2$ line at 5 K is 5 T, at 10 K is 4.3 T, at 15 K is 3.5 T, and at 20 K is 2.5 T. For this particular plasma synthesized boron powder, the wire was reacted in a hot isostatic press at 30 ksi and 950°C for 30 minutes to give a final density close to 90%. The transport data at 4.2 K (solid triangles) are rather close to the 5 K hysteresis data (solid squares) even though the hysteresis currents are flowing circumferentially and the transport currents are flowing axially. Many other wires showed close correlations between hysteresis and transport measurements.

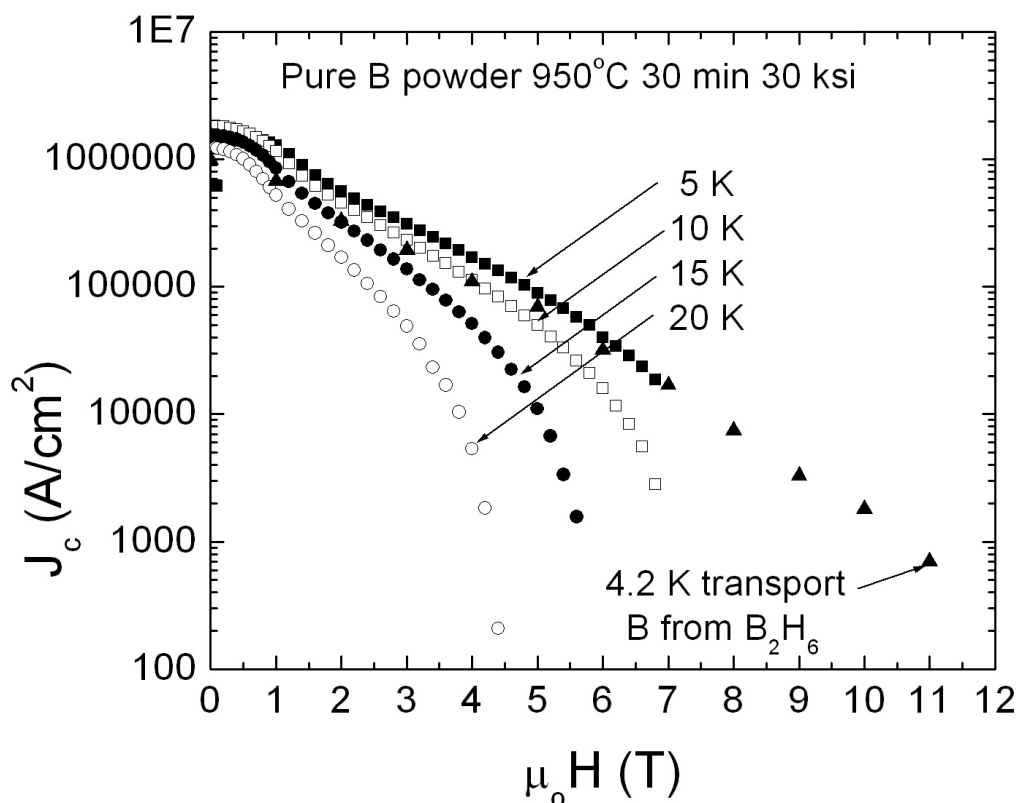


FIGURE 2. Temperature and magnetic field dependence of critical current density, J_c , for a wire reacted by hot isostatic pressing to a density of about 90% for the MgB_2 core. For comparison, transport data are shown for an 18 filament wire made with boron powder made from diborane.

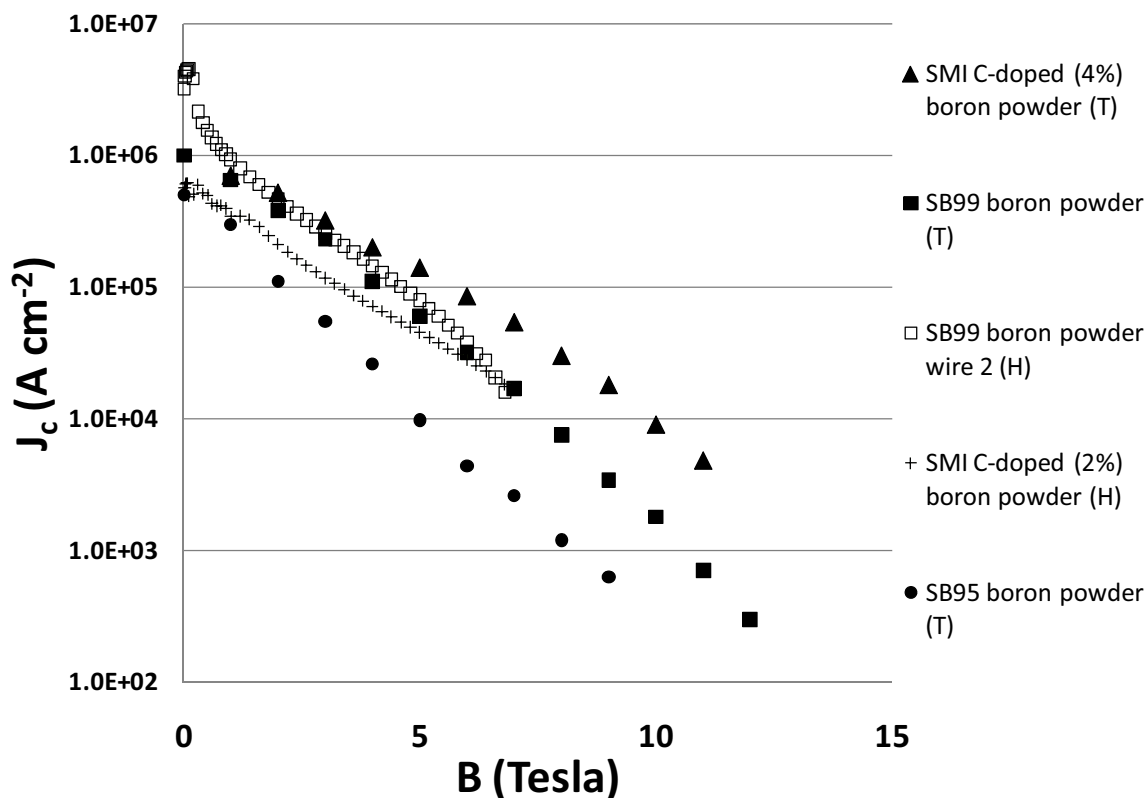


FIGURE 3. A comparison of wires made with several different batches of Specialty Materials powder with wires made with diborane derived boron, SB95 & SB99 (undoped powder, nominally 95% and 99% pure respectively). The “T” denotes transport measurements at 4.2 K and the “H” denotes hysteresis measurements at 5 K.

A more detailed comparison of our plasma synthesized boron powder with diborane boron is shown in Figure 3. The SB99 boron obtained from decomposing diborane is generally recognized to be very high quality amorphous boron powder, but is no longer available as a manufactured product. Even if someone were to once again produce the equivalent of SB99 commercially, diborane is very expensive, pyrophoric, and extremely hazardous to handle in large quantities, which would preclude its use as a raw material for many MgB_2 superconductor applications. The plasma synthesis process for boron powder was developed to produce high quality material that can perform comparably to powder made from diborane. RF plasma synthesis of boron is an electrodeless process [5] with the potential of producing higher purity material than a DC arc process in which electrode contamination can be problematic. Work reported by others [6] has shown that the quality of the boron precursor influences MgB_2 superconducting properties. Figure 3 indicates the boron powder made in this study can be used to make MgB_2 wire with performance characteristics that equal or exceed those made with SB99 [4]. The curve of J_c performance MgB_2 wire made with SMI 4% carbon-doped boron indicates that the wire maintains a current density of $>10^5 \text{ A cm}^{-2}$ up to magnetic field strengths of approximately 6 tesla.

Important questions remain regarding the preparation of these PIT wires. The wires consistently had a lower critical temperature, T_c , than MgB_2 made in pellet form from the same powder. Several wire fabrication parameters such as drawing conditions and the times and temperatures of the heating cycles need to be optimized in order to maximize the

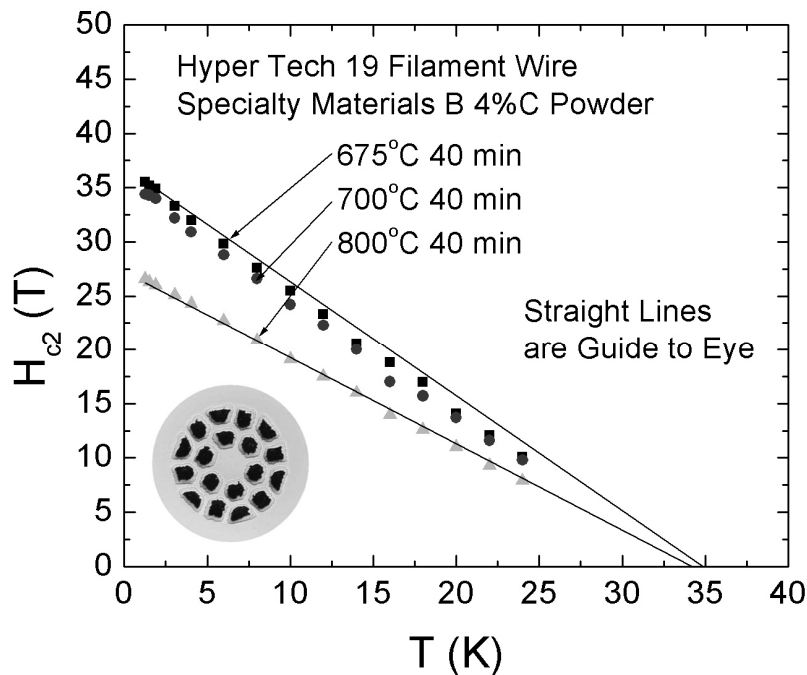


FIGURE 4. Upper critical magnetic field data for 19-filament PIT wire samples (inset shows ~ 2 mm diameter cross section) prepared from C-doped boron powder; the sample processed at 675°C shows $H_{c2}(T=0) \sim 37$ T

superconducting performance. Properties such as upper critical field, H_{c2} , can significantly depend on the wire processing temperature (Figure 4). The plasma synthesis process needs to be further investigated with the goal of producing boron powder with the optimal particle sizes, crystallinity, and dopant concentration for better MgB_2 superconducting wires. It should be pointed out that the powder mixing method used to make the C-doped wire shown in Figure 5 was different than that used for the C-doped wire shown in Figure 3, and resulted in different transport J_c data. Furthermore, Figure 5 shows that the addition of carbon dopant during the synthesis of boron powder [3] can enhance J_c at higher magnetic fields relative to wire made from undoped boron powder.

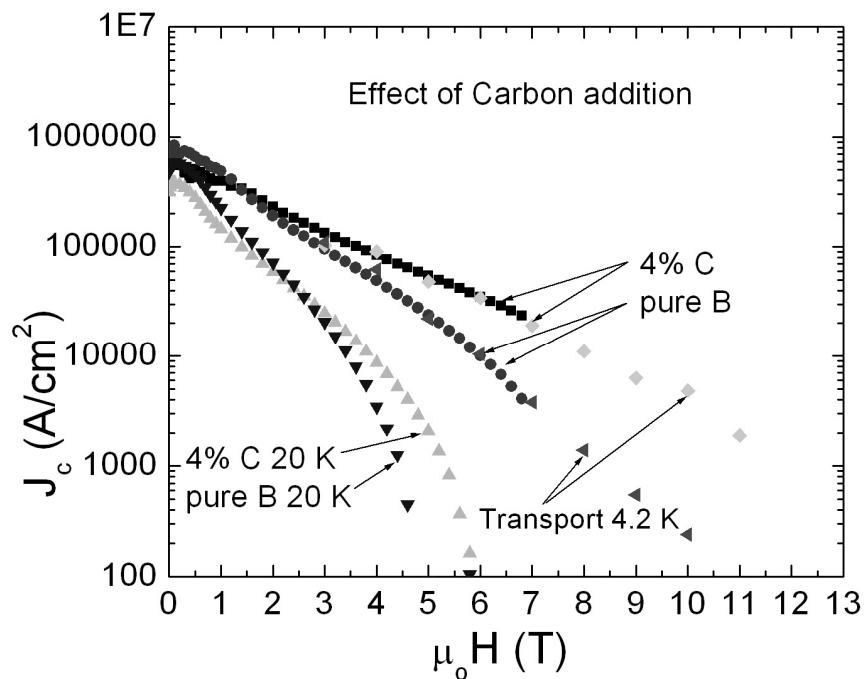


FIGURE 5. Comparison of critical current density for wires made with plasma synthesized boron nanopowders (undoped and 4% carbon doped); hysteresis data at 5 & 20 K go to 7 Tesla. Transport data at 4.2 K go to 11 Tesla.

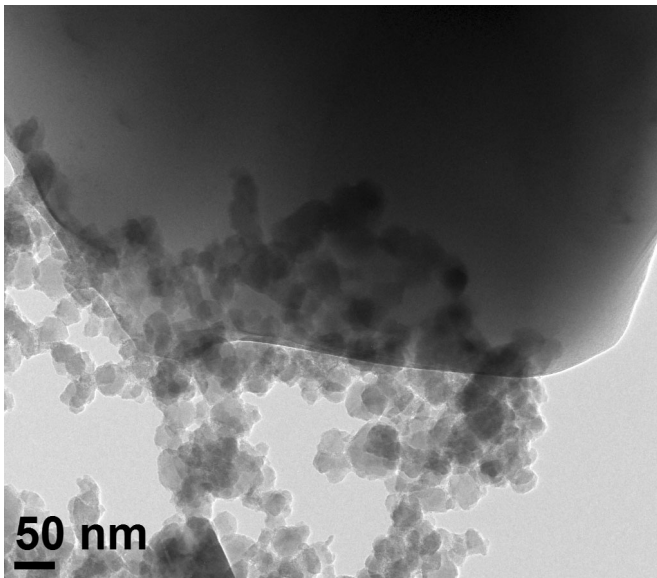


FIGURE 6. Transmission electron micrograph (TEM) of MgB_2 powder in a crush and float method that selects the small particles. Note that there is a full range of particle sizes from <20 nm to a micrometer. The large particles of $>1\mu m$ were floated away in the sample preparation so the small particles could be more easily seen.

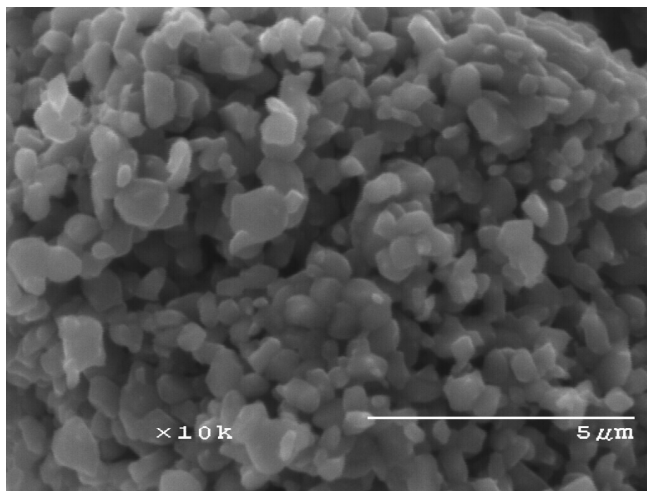


FIGURE 7. Scanning electron micrograph (SEM) of MgB_2 powder from the reaction of Mg vapor and nano-sized boron powder at $950^\circ C$. The micrograph shows a mixture of sub-micron and 1-2 micron particles.

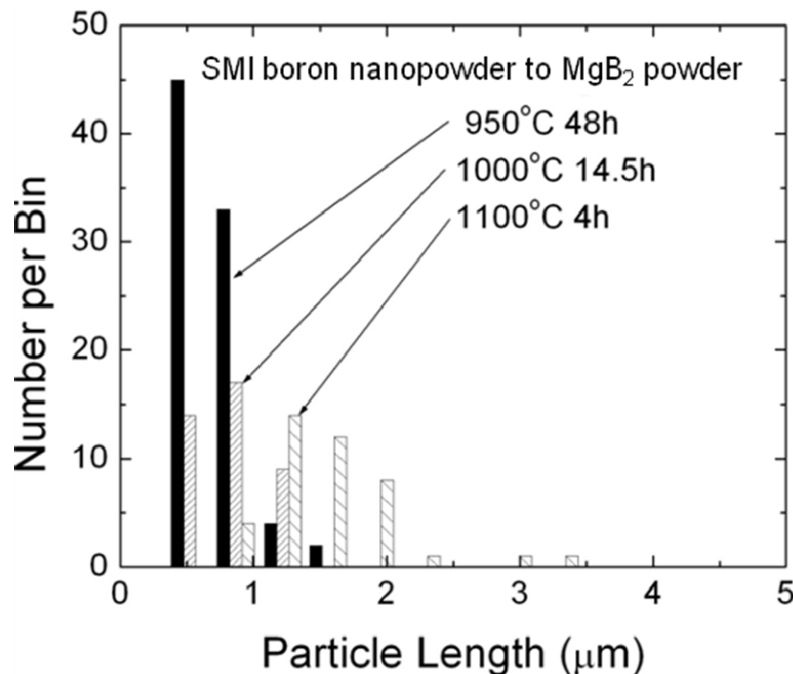


FIGURE 8. Histograms of MgB_2 particle sizes from SEM micrographs taken at 10,000X magnification. This data includes only particles ≥ 500 nm. There is a clear diminution of particle size of these larger particles with decreasing reaction temperature between the Mg vapor and the nano-sized boron powder.

MgB₂ powder from boron nano-sized powder

In an effort to find a satisfactory process for converting plasma synthesized boron into MgB₂ powder, a series of experimental runs were made in which the nano-sized boron powder was placed in the bottom of a cylindrical Ta tube with a Ta cup holding the liquid Mg above it. These were then sealed in quartz and reacted in a box furnace for different times and temperatures. Figure 6 shows a transmission electron micrograph when the resulting MgB₂ is observed in a crush and float method. The TEM micrograph shows that there is a significant fraction of nano-sized particles (<100 nm), but quantitative particle size distributions that include particles less than 500 nm have not been determined as yet. Figure 8 shows particle size histograms obtained from analyzing scanning electron micrographs such as that shown in Figure 7. Although these histograms include only larger particles (≥500 nm), they show that as the Mg + B reaction temperature is decreased, the particle sizes of the MgB₂ powder product also decreases.

CONCLUSIONS

The superconducting properties of *in-situ* MgB₂ wire made from SMI plasma synthesized boron powder were comparable to the best properties achieved to date in PIT MgB₂ wires using powder produced by the decomposition of diborane, B₂H₆ (SB99). Gas phase carbon doping increased the critical current densities substantially for fields above 4 Tesla. Preliminary attempts to prepare fine grain MgB₂ powder for an *ex-situ* PIT process were partially successful. A gas phase reaction of plasma synthesized boron powder and magnesium vapor requires higher temperatures and longer times to form MgB₂ than the solid state diffusion process used for *in-situ* wire. The growth of flat hexagonal grains of MgB₂ that are several micrometers across is clearly suppressed by using lower temperatures and longer times.

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REFERENCES

1. Vollath, D. J. *Nanopart. Res.* **10**, 39 (2008).
2. Marzik, J.V., Suplinskas R.J., Wilke, R.H.T., Canfield, P.A., Finnemore, D.K., Rindfleisch, M., Margolies, J., Hannahs, S.T. *Physica C*, **423**, pp 83-88 (2005)
3. Marzik, J.V., Lewis, R.C., Tillman, M.E., Wu, Y.Q., Finnemore, D.K., Rindfleisch, M., Tomsic, M., Yue, J., Croft, W.J., "Plasma Synthesized Boron Nano-sized Powder: The Effect of Processing Conditions on the Crystallographic and Microstructural Properties" in *Mater. Res. Soc. Symp. Proc.* 1148-PP12-01, Materials Research Society, Warrendale, Pennsylvania, 2009.
4. Sumption, M.D., Bhatia, M., Rindfleisch, M., Tomsic, M., and Collings, E.W. *Supercond. Sci. and Technol.* **19**, pp. 1550160 (2006).
5. Hamblyn S.M.L., Reuben B.B., and Thompson R., "Hydrogen reduction of boron trichloride to boron in an R.F. plasma", in "Special Ceramics 5: Proceedings of the Fifth Symposium on Special Ceramics held by the British Ceramic Research Association at Queens Road, Penkhull, Stoke on Trent on July 14, 15 and 16, 1970", British Ceramic Research Association, Stoke on Trent, 1972, pp. 147-155.
6. Chen, S.K., Yates, K.A., Blamire, M.G., and Driscoll, J.L. *Supercond. Sci. and Technol.* **18**, 1473 (2005).