Inert Gas Buffered Milling and Particle Size Separation of μm -Scale Superconducting Precursor Powders

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**Accelerator Technology Corp.
9701 Valley View Dr.
College Station, TX 77845
(979) 255-5531**

acctec@suddenlink.net

Satya Seshadri, PI

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Executive summary

The project developed an aerosol system for the wet milling and particle size separation of the precursor powders used in fabrication of powder-in-tube superconductors. The work builds upon the results of a previous SBIR-funded development that proved the basic principles of the virtual impactor (VI) technology and its efficacy for the powders of interest. The new project extended that work in three respects: it integrated provisions for recirculating the aerosol flow using inert gas to avoid contamination from O_2 , CO_2 and water in ambient air; a quad configuration of VI subassemblies to support kg/hr throughput; and it incorporated design features that eliminate error trajectories which would introduce trace contamination of larger particles into the separated flow.

The project demonstrated the technical effectiveness of the process and established its economic feasibility by achieving kg/hr throughput within a cost profile that would be profitable within the range of competitive toll fees.

The project is beneficial to the public through its potential to improve the performance of superconducting materials for research and for biomedicine. It also conveys potential benefits for powders used in high-performance ceramics (for example for engines for automobiles and for aircraft) and for high-performance electrical insulators for telecommunications circuitry.

Importance of powder size distribution in PIT superconductor

The powder-in-tube (PIT) process is used to fabricate high-performance multi-filament superconducting wires of Nb_3Sn [1], Bi-2212 [2], and MgB_2 [3,4]. While the specific powders, the synthesis routes, the sheath metal, and the PIT processing after powder filling are different in each case and indeed among the several practitioners of each superconductor, there is a common element that paces the ability to fabricate drawn multifilamentary composites of these materials. For high-energy physics applications the filament size is a critical parameter [5]. The PIT process entails cold-drawing the powder-filled tubes, restacking bundles of tubes, and repeated drawing and restacking to produce fine-filament round wire. The ultimate limit of this drawing and restacking comes when the tube apertures are reduced to $\sim$ twice the maximum particle size in the powder. Even if the frequency of such large particles is small, each occurrence of a break would result in rupture of the sheath and leakage of core material during subsequent heat treatment.

Most of the precursor powders for the above superconductors are ground using either jet-milling or attritor milling. Either technique produces a roughly Gaussian particle size distribution, with large-size tails extending to ~ 4 times the mean particle size. That large-size tail is a predominant limit for producing fine-filament superconducting wire using the PIT process. Particles in the size range up to cannot be removed by simple mechanical sieving (the fines aggregate electrostatically and block the sieve mesh) and techniques utilizing cyclones cannot separate below $\sim 10\text{ }\mu\text{m}$ size without passing large-size tails.

Virtual impactor sizing is the only technique that has the capability to provide near-zero-defect removal of particles above a chosen μm size threshold. The technique is illustrated in

Figure 1. The powder is dispersed as an aerosol suspension in a buffer gas. The aerosol is passed through a vane geometry in which 10% of the flow goes straight while 90% of it is forced to make an abrupt right-angle bend. The fate of each particle is determined by its Stokes flow. Large particles follow ballistic trajectories into the minor flow; small particles follow gas streamlines so that 90% go into the major flow.

Figure 1. Particle Separation in a Virtual Impactor

Development of VI Processing at ATC

In an earlier SBIR project [6] ATC developed a slot-geometry VI impactor and explored its performance and limits for use in the manufacture of precursor powders for PIT superconductors. Excellent separation with a sharp separation threshold was achieved. The detailed design of the slot-geometry impactor and the imaging of flow are summarized Ref. 7. Four issues were identified that needed to be addressed in order to adapt the process for cost-effective manufacture of the precursor powders for superconductors:

- Use inert buffer gas for the aerosol dispersion so that the powder is not exposed to oxygen, water vapor, or CO₂ during processing;
- Improve the powder dispersal system so that a larger mass loading of powder can be dispersed in the aerosol without aggregation;
- Introduce a powder-free boundary flow at the vane surfaces to eliminate particle interactions with the walls and velocity dispersion that could introduce trace impurities of large particles into the separated fines;
- Develop a more effective means of removing the fines from the separated aerosol flow.

The Phase 1 project had as its goals to develop solutions to the first three of these issues. A sealed-flow N₂ gas system was used to disperse the powder into a flow of nitrogen gas obtained from boil-off of liquid nitrogen. A fluidized-bed dispersal system was used to improve dispersal from 0.6 mg/liter obtained with a previous disperser to 14 mg/liter which is the limit at which particle-particle interactions would begin to interfere with separation. A boundary sheet flow of powder-free N₂ was injected along the vane surfaces so that powder particles in the convergent laminar flow do not encounter the region of velocity shear near the vanes and also cannot impact the vane surfaces. The Phase 1 project was extremely successful [8]:

✓ Excellent separation performance with four powders of importance for high-performance superconductors:

- Sn and Cu₅Sn₄ used by Supramagnetics in the fabrication of Nb₃Sn wire;
- MgH₂ used in the development of a new route for MgB₂ synthesis at Ohio State University;
- Mg flake used in fabrication of MgB₂ at Hypertech Research;
- MgB₂ powder that has been sintered and high-energy-milled at the UW Applied Superconductivity Center.

✓ A fluidized-bed dispersal system was effective in providing mass loading to 14 mg/liter with no evidence of aggregation.

✓ Integration of a boundary sheet flow of powder-free gas suppressed particle-wall interactions and preserved a sharp particle size separation up to large mass loadings.

✓ Sharp size separation was retained for mass loading up to 14 mg/liter, greater than any previous micron-scale aerosol separation process (see Ref. 9).

Interestingly the four powders that we obtained from superconducting material developers turned out to provide an excellent ‘acid test’ of the VI processing. One powder consisted almost entirely of ‘rocks’ much larger than the desired 2 μm cutpoint; VI processing removed *all* of the rocks. Another sample consisted almost entirely of fines; VI processing passed 90% of the fines.

Figure 2. Collection efficiency of fines in the minor flow, as a function of Stokes number.

Figure 3. Current density of Bi-2212 wire vs. filament size: the finer the powder, the greater the performance.

Figure 4. Quad virtual impactor with ~1 kg/hr mass flow capacity.

The goal of the Phase 2 effort was to develop such a scaled-up system incorporating two important additional features. First, a fluidized-bed jet mill is integrated into the system as the first stage, so that the powder can be further ground to any desired particle size distribution. Second, a recirculating gas system is integrated with the mill and VI separator so that an inert buffer gas can be used, thereby eliminating contamination from air constituents (H_2O , CO_2 , O_2). Third, the VI separator geometry was re-designed to accommodate kg/hr throughput. The optimum geometry that we chose is a quad-cylindrical VI array, shown in Figure 4. The system design and calculated performance are summarized in Ref. 10.

Construction of the Jet Mill/VI system

In Year 1 of the Phase 2 effort all components for the system were procured and/or built. A Netzsch Condux jet mill was procured for grinding the powder without introducing contamination, as shown in Figure 5. A Powerex quad scroll pump assembly is used to drive 50 l/s recirculating inert gas flow without contamination. Dry nitrogen gas is used, sourced from a pressure-builder Dewar.

The virtual impactor for the new system is configured as four subassemblies. Each subassembly contains a cylindrical slit geometry in which the flow enters from above, passes through a controlled slit geometry. 90% of flow is diverted through the right-angle slit, while 10% of the flow passes straight ahead. The components of the new quad VI unit are shown in Figure 6b.

Figure 5. Dr. Bhatia working on the jet mill and aerosol system.

Figure 6. VI subassemblies: a) one VI module; b) four modules assembled on base plate.

We devoted considerable effort to provide a suitable bag house to remove the powder from the aerosol flow after VI separation. In our earlier studies we had simply removed the powder on a filter paper disk, but for a volume production unit a proper bag house is required with capability for separating particles down to $<0.1\ \mu\text{m}$. We found a Torit filter capable of that separation, but no commercial bag house assemblies are capable of being evacuated, an essential step in our design to remove the ambient air from the system prior to filling with inert buffer gas. In the end we fabricated a housing for the two bag houses within a stainless steel vessel that was procured from an auction from a pharmaceutical manufacturer, shown in Figure 7.

Figure 7. a) Vacuum/pressure vessel to contain the two bag houses for the major and minor flows; b) detail of bag house inserts that will be connected to the peripheral top ports.

Plans for first operation

All components have now been completed and are being assembled at ATC, and the system is being prepared for commissioning.

The same superconductor developers and manufacturers who supplied powders for evaluation during our Phase 1 effort have supplied powders that we will use in evaluating the performance of the upgraded milling/VI system. We will study performance for milling and separation of NbSn₂, Nb₆Sn₅, Mg, and Bi-2212 powders. Two research groups and three superconductor manufacturers are awaiting our processing of their powder samples.

New application for first product: Phase-pure amorphous boron for MgB₂

Subsequent to the sequence of SBIR grants reported here, ATC was awarded a Phase 1 grant to develop rf plasma torch synthesis of MgB₂ superconducting powder. Its overall objective is to develop a way to introduce homogeneous alloying of C and SiC impurities into phase-pure MgB₂. Several groups have attained remarkable benefits from such alloying in raising the upper critical field H_{c2} from ~14 T to ~30 T (bulk) and ~50 T (thin films). But *no one* has succeeded in producing that benefit homogeneously, so that current transport in a practical powder-in-tube (PIT) conductor is largely the same as without the alloying.

ATC has conceived the possibility of attaining such homogeneity by passing aerosol suspensions of reactant powders through an rf plasma torch, with each reactant transported on a streamline that heats it to an optimum temperature for the synthesis reaction [11]. This procedure would uniquely access non-equilibrium kinetics for the synthesis reaction, and would provide the possibility to separately control the temperature and stoichiometry of each reactant as it enters the mixing region where synthesis occurs. It also facilitates the introduction of seed particles (*e.g.* nanoscale SiC) to dramatically enhance the rate of the synthesis reaction compared to gas-phase synthesis in rf plasma reported by Canfield and others.

Because this new effort directly utilizes the aerosol technology for jet milling and size separating powders developed under the grants for which this is the final report, the results from this subsequent effort are reported below. Indeed these results are likely to produce the first manufactured product for our R&D: nanoscale phase-pure amorphous boron powder.

ATC commissioned a 60 kW 5 MHz rf source for a manufacturing-scale rf plasma torch. This effort required repair of numerous elements, integration of cooling and input circuits, and tuning of the load characteristics. The effort was successful, and the source has now been tested to ~full power (Figure 8).

Also in the Phase 1 effort we encountered a subsidiary but very important problem: the world is running out of the only present supply of phase-pure amorphous boron. The starting boron powder must be in the amorphous phase in order for the synthesis reaction to produce phase-pure MgB₂. Even small contamination with crystalline boron results in the formation of parasitic phases such as MgB₄, MgB₇, *etc.* Such parasitic phases are a primary element of the connectivity problem, in which even though a sample powder may contain grains of high-quality MgB₂, adjacent grains are surrounded by intergrowths of parasitic phases so that current transport is badly degraded.

The best results to date have been obtained using boron powder produced long ago for a rocket propellant development project. The synthesis process was complex and is now largely lost, and the manufacturing equipment has long since been scrapped. The last batch of the powder has been used during recent years to support MgB_2 R&D at several labs, but supplies are dwindling.

ATC has identified a first application of its plasma torch to synthesize phase-pure amorphous boron flake using a rapid-quench splat technique. Inexpensive technical-grade boron would be purified of contaminants, then dispersed as an aerosol in inert gas and passed through the plasma torch to melt it into a spray. The spray would be splat-condensed on a rotating drum to form pure amorphous flake.

The process would begin with technical-grade boron powder, having good stoichiometric purity, nanoscale particles, but significant contamination of MgO and crystalline boron. We used wet chemistry to remove the MgO impurity, and analyzed the phase composition using X-ray diffraction (XRD) (Figure 9) and the particle size distribution using a Coulter counter (Figure 10). The next step will be to build an rf plasma torch (Figure 12) with a recirculating single-component aerosol feed and the cooled splat drum and collector (Figure 14), and undertake process development for amorphous boron powder.

This revised goal has two benefits. First, it is an easier technology than our ultimate goal of a multi-component laminar flow torch. We have been counseled by those experienced in plasma torch technology that our ultimate goal will require a torch that *should* be feasible but has never been attempted. It may require an extended period of R&D for both the torch itself and the gas dynamics in the reaction region.

Second, this simpler single-component process will yield a product powder that is important today for the many groups undertaking powder-metallurgy routes to MgB_2 . ATC should be able to commence delivery of phase-pure amorphous boron powder as a product by the end of its Phase 2 effort. The cash flow from that product could help us to continue into the more demanding multi-component plasma synthesis process for C-loaded MgB_2 synthesis.

The above success and learning curve has brought us to a significant shift of strategy from what was originally set out in the Phase 1 plan. But this shift has brought us to within sight of a powder product that will itself be an enabling boost for the community of MgB_2 developers.

Figure 8. 60 kW 5 MHz rf power supply commissioned for operation of rf plasma torch.

Figure 9. X-ray diffraction pattern showing the lines from boron powders before and after wet processing.

Figure 10. Particle size distribution in boron powder.

Figure 11. Critical current vs. field measured in monofilament wire made using MgB_2 synthesized from boron powder: small enhancement from removing MgO residues.

Figure 12. rf plasma torch: a) cross-section showing rf field distribution; b) simple torch in operation; c) modeling using Fluent MHD module [2, 3].

Figure 13. Design parameters for modeling of rf plasma torch.

Figure 14. Schematic layout for rf plasma torch synthesis of phase-pure amorphous boron.

The importance of pure-amorphous boron to make single-phase MgB₂

Shown in Figure 15 are the variations of transport current with applied field (at 6K and 20K) for four different samples of MgB₂ prepared using four different boron powders namely C98 (Alfa-Aesar, 98% pure, crystalline), C99 (FluoroChem, 99% pure, crystalline), A9597 (Fluka, 95-97% pure, amorphous) and A9999 (Alfa-Aesar, 99.9% pure, amorphous). Details of the powders and particle sizes are presented in Table 1 [1]. While Figure 2 shows the microstructures of the resulting MgB₂ made from the above mentioned powders. It is evident from the two figures that the resulting microstructure and transport properties of MgB₂ are highly depended on the starting boron precursor powder.

Table 1. Specifications for different commercial Boron powders.

Boron powder	Source	Form	Purity	Peak value(s) of particle size distribution (μm)
B-C98	Alfa Aesar	Crystalline	98 %	21.10 [325 mesh]
*B-C99	FluoroChem	Crystalline	99 %	11.42, 0.56 [< 40 μm]
*B-A9597	Fluka	Amorphous	95 – 97 %	0.56, 2.42 [-]
B-A9999	Alfa Aesar	Amorphous	99.99%	0.54 [325 mesh]

From Figure 15 it is clearly seen that MgB_2 samples made from amorphous Boron powder are far superior in the properties as compared to crystalline Boron samples. Even the sample made from less pure amorphous boron showed better properties than the purer crystalline boron sample. The exact reason for the fact is though not yet completely understood still one of the possible reasons can be directly related to the fact that as compared to amorphous boron, the crystalline boron, which is in most of the cases in the β -rhombohedral phase, has a lower reactivity and allows slower Mg diffusion. Since, the formation reaction of MgB_2 involves inward diffusion of Mg in boron and reaction at the interface and therefore the above mentioned slow diffusivity and lower reactivity would lead to the formation of leftover intermediate non-superconducting phases in the final product. This has been observed in certain cases.[4-6].

Commercial amorphous boron, even-though claimed to be amorphous still contains a small percentage of crystalline phase as shown in the XRD below (Figure 16). ATC's rf-plasma synthesis technique has the potential to prepare phase-pure nanosize amorphous boron powder.

Figure 15. Characterization of MgB_2 samples prepared using four different kinds of boron: a) j_c vs. T ; microstructure.

Figure 16 XRD pattern for different kinds of commercial boron powders (Peaks shown with the dotted lines are B_2O_3 phase)

Figure 17. Microstructure of boron powder: a) before cleaning, showing intergrain residues of MgO; b) after wet-cleaning to remove Mg.

Presence of MgO in starting Boron Precursor

Another important observed difference between the high performing and mediocre quality MgB_2 superconductors has been the presence of large amount of MgO in the final microstructure. This insulating MgO, shown in blue circles in Figure 17a, resides on the grain boundaries and reduces the effective current carrying cross-section thus limiting the capabilities of the MgB_2 strand [7]. One of the important sources of this very stable MgO is the Boron precursor powder. Most of the boron powder is prepared by the reduction of B_2O_3 by Mg and hence MgO is a major impurity in final boron powder (~50% of the total impurity content). ATC, with its proposed plan would be able prepare Boron powder with almost none to very less quantity of MgO impurity phase.

Presence of B_2O_3 in starting Boron precursor

Apart from MgO another major impurity in the commercial boron is B_2O_3 . The presence of this B_2O_3 phase is also detrimental for the reason that during the MgB_2 preparation this B_2O_3 can be reduced by Mg and lead to the formation of the above mentioned MgO phase and therefore removal of B_2O_3 from B is important. Figure 17b shows the micrograph of a MgB_2 sample [7] prepared in the exact same conditions as Figure 17a but after removing MgO and B_2O_3 .

Particle (agglomerate) size of starting Boron Powder

Another important factor affecting the properties of MgB_2 superconducting strands is the starting particle sizes of the precursor powders specially boron because of the above mentioned fact that MgB_2 is formed by the inward diffusion of Mg in boron particle followed by the reaction. Therefore, the final grain size of MgB_2 is directly related to the starting Boron particle size as shown in the microstructure in Figure 2. The boron powder for injection in the plasma torch melt-splat process will be prepared using ATC's jet-mill coupled with virtual-impactor size separation. It has been shown by various previous research studies that reducing the particle size of starting boron has beneficial effects on the superconducting properties of MgB_2 . [8]

Conclusion

In summary ATC is pleased to report that we have successfully developed an aerosol system that will provide jet milling to micron particle size, followed by particle size separation to remove all particles larger than a target size threshold, in a recirculating inert gas flow. The system is capable of processing ~1 kg/hr throughput, depending upon the density of the powder and the size threshold desired. The final assemblies are being completed at the time of this report, and commissioning should be done during summer 2008. Sample precursor powders of Nb₃Sn, Bi-2212, and MgB₂ have been obtained from several clients, and the system will be evaluated in its processing of those samples. A first application with potential for commercial sales has been identified, in which the aerosol system will be integrated with an rf plasma torch to synthesize phase-pure amorphous boron powder using a splat-melt process. If successful it would be only source for such material, with potential benefits for development of homogeneous MgB₂ superconductor and other materials applications.

References

- 1 J.L.H. Lindenhovius *et al.*, 'Powder-in-tube (PIT) Nb₃Sn conductors for high-field magnets', IEEE Trans. on Applied Superconductivity **10**:1, 975-978 (2000).
- 2 A. Matsumoto *et al.*, 'Improvement of the microstructure and critical current densities of Bi-2212 round wires with a precisely controlled heat treatment', Supercond. Sci. Technol. **17**, 989-992 (2004).
- H. Miao *et al.*, 'Development of round multi-filament Bi-2212/Ag wires for high-field magnet applications', IEEE Trans. on Appl. Superconductivity **15**:2, 2554 (2005).
- 3 B.J. Senkowicz *et al.*, 'Strongly enhanced H_{c2} by high energy milling of C into MgB₂, Proc. CEC-ICMC Conference, Keystone, CO, Aug. 29-Sept.2, 2006.
- 4 M. Sumption *et al.*, 'High critical current density in NbCu-alloy sheathed MgB₂ multifilament superconducting strands', *ibid.*
- 5 Finley, D. et al., 'Time dependent chromaticity changes in the Tevatron', Proc. Particle Accel. Conf. (PAC87), Washington, DC, IEEE Cat#: 87CH2387-9, p. 151 (1987).
- S. Sanfilippo, 'Persistent and coupling current effects in the LHC superconducting dipoles', IEEE Trans. Appl. Superconductivity **13**:2, 1239 (2003).
- 6 X. Fu, A. Gupta, P. McIntyre, and D. Phares, 'New size sorting technology for superconducting powders', IEEE Trans. Appl. Superconductivity **13**:2, 3494 (2003).
- 7 S. Seshadri *et al.*, 'Performance of a slit virtual impactor operated at high mass loading', J. Aerosol Sci. **36**, 541 (2005).
- 8 X. Fu et al, 'Removal of supramicron particles from precursor powders for PIT fabrication of Nb₃Sn and Bi-2212 multifilament superconductors', IEEE Trans. Appl. Superconductivity **15**:2, 3510 (2005).
- 9 T.K. Kim *et al.*, 'Visualization of defect particle transmission to the major flow of a slit virtual impactor', Aerosol Science and Technology **38**, 870 (2004).
- 10 A. McFarlane, P. McIntyre, and S. Seshadri, 'Virtual impact fractionation of superconductor precursor powders in inert gas atmosphere', IEEE Trans. Appl. Superconductivity **17**:2, 2576 (2007).
- ¹¹ T. Elliott, P. McIntyre, and A. Sattarov, 'Optimizing plasma synthesis for 'dirty'MgB₂', IEEE Trans. Appl. Superconductivity **17**:2, 2922 (2007).