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PRODUCTION OF SUPERCONDUCTOR/CARBON BICOMPONENT FIBERS

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Superconductor/carbon bicomponent fibers have been prepared by filling specially produced C-shaped carbon fibers with a suspension of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ powders. The bicomponent fibers were processed in an inert atmosphere to retain the strength and flexibility of the carbon backbone. However, reactions between the carbon fiber and the oxygen content of the superconductor were observed. In response to this problem, metallic layers were physically evaporated onto the carbon surface, and the fibers were converted to metal oxides, carbides, and nitrides. Superconductor/ceramic bicomponent fibers were then prepared by filling the ceramic fiber with the superconductive suspension and processing in oxidizing atmospheres.

Certain materials are unable to be drawn or spun into fiber form due to their improper melting characteristics or brittleness. However, fibrous samples of such materials are often necessary for the fabrication of intricate shapes and composites. In response to this problem, researchers at Clemson University developed and patented a unique process, referred to as the "piggyback process", to prepare fibrous samples of a variety of non-spinnable ceramics.¹ In this technique, specially produced C-shaped carbon fibers serve as "micromolds" to hold the desired materials prior to sintering. Depending on the sintering atmosphere used, bicomponent or single component fibers result. Alumina, zirconia, silica, and silicon carbide fibers have been produced by this process.

While much has been demonstrated worldwide concerning the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor, fabrication into unique forms such as fibers and composites has proven quite difficult. Researchers at Clemson University are currently investigating the feasibility of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ fiber production by the piggyback process. Fibrous

superconductor samples would offer the potential advantages of improved flexibility, enhanced critical current density, and unlimited shape formulation through composite development. Multifilamentary composites could be formed using a suitable polymer or metallic matrix, which could be drawn into wires or pultruded into a variety of shapes to meet unique design constraints.

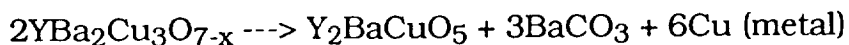
The carbon fibers employed for this research were melt-spun in house from petroleum pitch, oxidized, and carbonized to produce high purity fibers with an approximate web distance of 30 microns. The fibers were attenuated into segments of 1-2 inches. The $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ powders were prepared by solid state sintering of Y_2O_3 , BaCO_3 , and CuO and were determined phase pure by X-ray diffraction and a standard four-probe resistivity measurement. An average transition temperature of 90K was obtained.

The carbon fibers were filled with the superconducting material by dipping the fibers into a well-dispersed organic suspension of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ powders and evaporating the solvent. Due to the small web distance of the fibers, careful control of the particle size distribution of the superconducting powders was essential for proper particle packing and improved density of the sintered sample. An optimum distribution consisted of particles between 10 and 0.2 microns.

The filled fibers were subjected to low temperature firings (< 450°C) in air or oxygen to burn out the remaining organics. To retain the carbon backbone, the bicomponent fibers were subsequently heated in an inert atmosphere to 950°C to properly sinter the ceramic. Thermogravimetric analyses showed that a significant amount of oxygen was lost from the superconducting structure during inert atmosphere processing. Although a similar oxygen loss was exhibited from samples processed in oxidizing

atmospheres, the loss was reversible during slow cooling, with the majority of oxygen regained in the temperature range of 700°C-400°C depending on the oxygen partial pressure.² As unprotected carbon can withstand up to 450°C in oxidizing atmospheres, a low temperature anneal in flowing oxygen was employed to restore the oxygen content to the superconducting structure. A superconductor/carbon bicomponent fiber is shown in Figure 1.

However, the oxygen released from the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ compound at high temperatures reacted with the unprotected carbon fiber, resulting in the formation of a carbon monoxide atmosphere along the interfacial area. The presence of carbon monoxide served to further reduce the superconductor over time. Due to their unique valency configuration, the copper ions were found to reduce most readily according to the following decomposition reaction³:



To prevent oxygen loss to the carbon fiber, a variety of potential oxygen diffusion barriers have been examined to determine their effectiveness. The important parameters included oxygen permeability, chemical reactivity, and thermal expansion properties.

A variety of techniques were considered for depositing the thin barrier layers onto the carbon fiber surface. Sol-gel precursors of alumina, zirconia, and barium titanate were used to coat several fiber batches. Although the use of sol-gels allowed for decreased sintering temperature and more homogeneous products, high porosity and large shrinkages resulted, leaving large gaps in the coating for oxygen diffusion.

Metal barrier layers were deposited by sputtering, electroless plating (Enthone Corp), and physical vapor deposition. Sputtering

produced coatings of uniform thicknesses, but the coating was extremely porous and offered little protection against oxygen diffusion. Electroless coatings of nickel and copper were uniformly deposited, but the nickel and copper formed oxides during processing, reacting with the superconductor and also reducing the structure. Physical vapor deposition offered the advantages of more reliable thickness control and unlimited metal selection.

Although easy to deposit onto the fibers, metals exhibit high coefficients of thermal expansion (CTE's). The net CTE for the carbon fiber is $1 \times 10^{-6}/^{\circ}\text{C}$, while the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ material possesses a net CTE of $\sim 13 \times 10^{-6}/^{\circ}\text{C}$. This difference in thermal expansion results in shrinkage of the superconductor material away from the fiber (See Figure 2). Metal oxides, carbides, and nitrides typically possess lower CTE values. To produce coatings of these materials, the deposited metals were converted to the desired compound by controlling the sintering atmosphere. Fibers produced to date by this technique include silicon carbide, silicon nitride, nickel carbide, and alumina. The fibers were totally converted to the desired compound, and the C-shape remained intact.

These ceramic fibers can withstand the required sintering temperature for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ in oxidizing atmospheres, eliminating the need for inert atmosphere processing. All oxygen lost during heat-up can be easily regained during slow cooling. Although not as flexible as the carbon backbone, the ceramic fibers do alleviate the thermal expansion mismatch, while providing sufficient strength to protect the superconductor during processing and handling.

Prepared fibers have been analyzed for composition and structure using a Debye-Scherrer camera for small sample X-ray diffraction. Most samples processed without diffusion barriers exhibited the oxygen-deficient tetragonal phase of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$.

However, the orthorhombic and tetragonal phases may have coexisted in some samples, preventing the drop in electrical resistivity indicative of superconductivity.⁴ Preliminary samples prepared with the diffusion barriers and processed in oxidizing atmospheres have possessed the orthorhombic phase.

Four point probe electrical measurements of the fibers have proven quite difficult. Small microcracks have been discovered by electron microscopy, resulting from the thermal expansion mismatch and improper handling of the fibers after processing. In addition, the fibers produced have proved to be only partially sintered (i.e. $\leq 50\%$ theoretical density), leading to a drastic decrease in critical current density and potentially prohibiting current flow completely. The low density of the fibers also contributes to their poor mechanical strength. While the feasibility of the piggyback process for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ fiber production has been demonstrated, much work is still necessary to improve the quality of the sintered material if the fibers produced are to be incorporated into useful composites or cables.

Acknowledgements

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References

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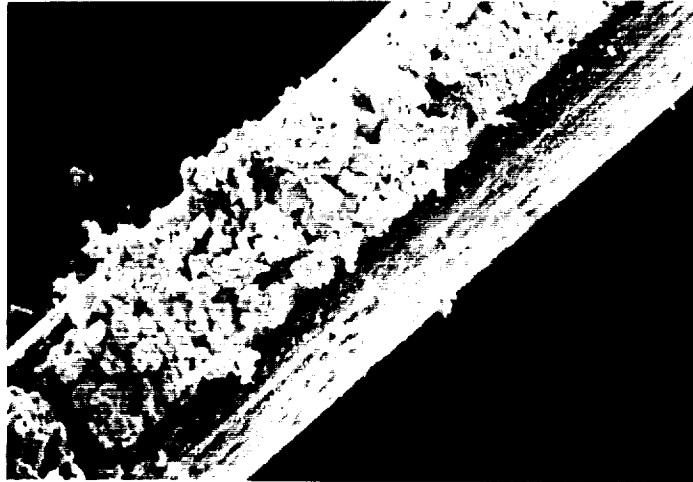


Figure 1: Superconductor/carbon bicomponent fiber.

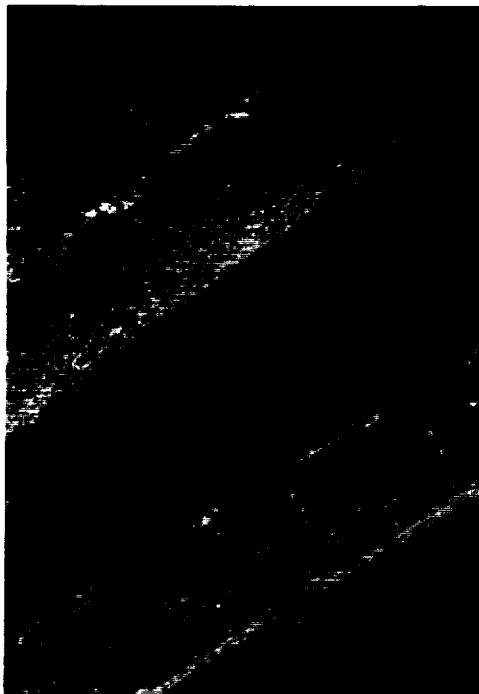


Figure 2: The thermal expansion mismatch between the carbon fiber and the superconductor result in shrinkage of the ceramic away from the mold.