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Abstract

The requirement of high critical current density has prompted extensive research on ceramic processing of high-T_C superconductors. An overview of wire fabrication techniques and the limitations they impose on component design will be presented. The effects of processing on microstructure and critical current density will also be discussed. Particle alignment has been observed in extruded samples which is attributed to high shear stresses during plastic forming. Composites of superconductor and silver in several configurations have been made with little deleterious effect on the superconducting properties.

Introduction:

Superconductivity above liquid nitrogen temperature (77K) is of great interest for many applications. Advantages over superconductors that operate at liquid helium temperature include less complicated refrigeration systems and the low cost of liquid nitrogen. Several oxide systems have demonstrated the ability to superconduct at temperatures above 90 K. The Y-Ba-Cu-O system has been widely studied for over one year [1], and the effects of processing on properties remains a subject of current research. The Bi-Sr-Ca-Cu-O and Tl-Ca-Ba-Cu-O systems have been recently discovered, and have transition temperatures above 100 K [2-3]. Conductor fabrication from the bismuth compound may be difficult due to its highly micaceous microstructure and low densities achieved by conventional sintering processes [4]. Initial experiments show that the thallium compound is especially promising owing to high critical current densities in poorly sintered specimens [5] , although the toxicity of thallium may hinder its use in some applications.

Potential uses for high-T_c superconductors include power generation and storage, medical diagnostics, transportation, large magnets, and microelectronics [6-7]. Bulk and composite superconductors in the form of wires and tapes are candidates for a wide array of potential applications. Large scale implementation will involve fabrication of conducting rings for magnetic energy storage, windings for power generation, and long continuous wire for power transmission lines.

Mechanical and electrical properties must be optimized before implementation of these ceramic materials into actual components. The bending radius of a brittle high-T_c wire is limited by the wire radius and the fracture toughness of the material [8]. Proper materials processing in order to decrease the critical flaw size will assist in increasing wire flexibility. The critical transport current, J_c, and the upper critical magnetic field, H_{c2}, are also important material parameters for operational components made of $YBa_2Cu_3O_{7-x}$ (herein designated YBCO) [9]. Practical wire applications will necessitate a critical current density on the order of 10,000 A/cm^2 in magnetic fields up to 5 Tesla [10].

Superconductors have a finite resistance for alternating current. However, their resistances may be lower than those metallic conductors. Microelectronics and other high frequency applications may benefit by the lower resistive losses offered by superconductors. High quality thin films of YBCO have been shown to have critical current densities on the order of 10^5 A/cm^2 [11], and may be viable for transmission lines in microelectronic circuitry. Cooling monolithic circuits down to liquid nitrogen temperatures results not only in superconducting interconnects, but also increases transistor performance by increasing carrier mobility [12]. Picosecond pulse propagation of patterned YBCO tranmission lines on yttria stabilized zirconia substrates has been studied, and low signal distortion was demonstrated [13]. This is a positive step toward the development of high speed interconnects. Materials requirements for high power rf cavities have been studied for particle beam accelerator applications [14]. Low surface resistance must be maintained in large magnetic fields. Other considerations include local heating of the superconductor, environmental attack of the superconducting surface, and compatibility of the oxide superconductor with other materials. Other possible high-frequency applications include narrow band filters, stabilized oscillators, and directive antennas [15]. Electromagnetic shielding materials for biomedical applications may be an early application for high-T_c materials [16].

Fabrication Techniques for Bulk Wire:

In comparison with single crystals and thin films, the primary deficiency for fabrication of bulk ceramic YBCO is the low critical current density. Novel processing methods have been used to increase the critical current density. Jin et al. produced a polycrystalline sample by a melt-texture growth technique that has a large J_c (7400 A/cm^2) [17], and recently reported a J_c of 17,000 [18]. These samples are characterized by needle-shaped grains (40-600 μm length) with the long dimension parallel to the conduction direction. Kohno and coworkers obtained high density powder packing by swaging YBCO powder in a silver tube [19]. The silver sheath was dissolved in nitric acid, and the YBCO core was sintered to obtain a wire with a J_c of 3900 A/cm^2. Similar results were obtained by rolling the superconductor in silver to obtain fired densities of 92%, and critical current densities as high as 3330 A/cm^2 were measured [20].

A versatile technique for forming continuous lengths of wire is plastic extrusion.

Fabrication of bulk superconducting wires by extrustion is summarized on Figure 1. The process originates with a well characterized YBCO powder, and synthesis may be carried out by a variety of methods. The mixed oxide route is the most common synthesis technique, although chemical routes such as controlled precipitation and sol-gel have the advantage of better control particle size and distribution [21].

In this study, precursor powders of $BaCO_3$, Y_2O_3, and CuO were mixed in stoichiometric amounts and pressed into disks for calcination. The calcination temperature was 890 °C for a duration of 16 hours, and the disks were crushed after firing. Powder calcination is a complex process due to low melting eutectics and residual $BaCO_3$, and several heat treatments were necessary to obtain the proper YBCO phase [22]. The procedure was repeated 4 times to produce a powder that was phase pure in accordance with x-ray powder diffraction patterns. Commercial YBCO powder (Rhône-Poulenc Inc.) was also used in the fabrication of extrusioned wire.

The final particle size and morphology will affect all of the subsequent processing operations. Milling operations were carried out to achieve the desired particle size and distribution. The calcined powder was jet milled to an median particle size of 2.4 µm. Scanning electron microscopy revealed the particles to be platelike.

In the plastic forming process, the YBCO powder is combined with a set of organics, and is mixed in a twin screw blender for optimal homogeniety. A solvent provides the basic vehicle into which the oxide powder and other organics are placed. Care must be taken in selecting a solvent that is compatible with the YBCO powder and the other organic constituents. Water is not a suitable solvent because of barium dissolution [23]. Typical organic solvents include methyl ethyl ketone, methanol, or xylene. Dispersants are used to deflocculate the inorganic particles in the solvent, and to assist in obtaining higher green densities. Binders impart strength to the green body, and plasticizers promote flexibility.

The extrusion process consists of placing a large pressure (approximately 20 MPa) on the plastic mass and forcing it through a small aperture. Wire with radii between 0.1 and 1.5 mm have been manufactured in lengths well over 200 cm. The wire had great flexibility in the unfired state and 3 cm diamater coils of 5 to 10 turns have been fabricated. Some degree of particle alignment can occur due to the high shear stresses induced during the process. Texturing may enhance the critical current density because of the anisotropic transport properties observed in YBCO [24]

Heating the extruded wire is necessary for powder consolidation. The heat treatment schedule for fabricated shapes is divided into three basic sections as shown in Figure 2. The entire procedure is generally carried out in flowing oxygen. Initially, a slow increase in temperature is required to remove organics from the green body. If the organic are removed rapidly, the final product will have large voids, and have a bloated appearance. Sintering a well calcined powder will induce formation of a liquid phase at a temperature between 930-960 °C [25]. The onset temperature of the melting is dependent upon the partial pressure of oxygen. The liquid phase is utilized extensively to achieve dense samples. The final step is an annealing procedure to incorporate oxygen into the YBCO lattice to form the superconducting phase. The relationship between oxygen content and phase transition to the superconducting orthorhombic phase has been studied extensively [26].

For many applications, the high-T_c superconductor must be bonded to a normal conductor. If the superconductor should quench, then the current will shunt across the normal conductor. The generated thermal energy can also be removed from the superconductor by a good thermal conductor to prevent quenching. High power cavity applications will also require that the superconductor be in contact with a thermal conductor such as a metal.

Co-processing of materials will entail interfacial studies between superconductor and substrate materials. A strong bond will usually result when there is a small amount of interdiffusion, although excessive diffusion of the substrate material into the superconductor may result in property degradation. Mismatch in thermal expansion coefficients will result in cracking or spalling of the superconductor. The thermal expansion coefficient for common substrate materials is shown in Table 1.

The thermal expansion coefficient of YBCO (13 x10 $^{-6}$ °C^{-1}) is larger than most of the oxide materials listed in Table 1, and the phase transition between 500 and 700 °C results in an anomolous thermal expansion coefficient (32 x10 $^{-6}$ °C^{-1}) [27]. The large difference has been shown to produce cracking, and very low expansion materials such as amorphous silica may be difficult to use for a substrate. It may be pointed out the the high thermal expansion of metals shown on Table 1 may provide the desired compatibility of thermal expansion coefficients. If the substrate material has a higher thermal expansion coefficient than the superconductor, then upon cooling the coating will be in compression. Oxide materials tend to be stronger in compression than in tension, and hence such a match in thermal expansion coefficient may prove beneficial. Several processes have been developed for depositing films of YBCO superconductor onto various substrates [11,14,21,30,31].

Properties and Microstructure

Direct current and rf properties were measured on samples of YBCO fabricated by extrusion and thick film techniques. Direct current measurement of the transition temperature and critical current density were carried out by a four point probe technique. Surface resistance in the MHz range measurements were made in a half wave resonant cavity.

Final densities of the extruded specimiens were 85 percent of theoretical (6.3 g/cm^3) at sintering temperatures of 950 °C. Texturing has been studied in these extruded samples that have been characterized previously by scanning electron microscopy and x-ray analysis [8] [24]. The grains have a large aspect ratio with average lengths of 20 microns and widths of 5 microns.

The extruded specimens of YBCO have superconducting transition temperatures of 91 K, and transition widths of 1.1 K. The transition temperature has been found unchanged when silver is incorporated into a superconductin matrix [32]. Critical current densities for extruded wires range from 60 to 650 A/cm^2 , and are significantly smaller than those reported for thin films that have J_c's in excess of 10^5 A/cm^2 [11]. The J_c also decreases with increasing magnetic field, and therefore improvement is required before extruded high T_c wire can be incorporated into a practical device.

Resonant cavity measurements of extruded wire samples show that the rf surface resistivity is an order of magnitide less than for copper at 77 K. The surface resistance and increases significantly as the power and frequency are increased [33], and becomes equivalent to that of copper at a frequencies about 3 GHz and surface magnetic fields of 2 Gauss. Smilar results have been observed with superconducting thick films coated on silver wire.

The exact mechanism for the limitation of critical current in bulk samples has not been determined, and several possibilities have been suggested. As seen from the work of Jin and co-workers [17,18], the microstructure plays an important role in the electrical properties. Enhancement of J_c has been correlated with particle orientation, removal of grain boundary phases, and increased density. Spurious phases at the grain boundary may inhibit current flow between superconducting grains. Non-superconducting second phases such as barium cuprate at the grain boundaries are due to liquid phase formation during sintering, and an immediate challenge is to produce a dense sample without the aid of a liquid phase. Samples that contain porosity may also reduce the number of current paths and increase susceptibility to environmental attack. Carbon has been observed at the grain boundary, which has been attributed to the incorporation of carbon environmental contamination [34]. Microcracks may also form owing to a large anisotropy in the thermal expansion coefficient of YBCO [35]. The oxygen assisted transformation from tetragonal to superconducting orthorhombic phase may also be hindered by the rate of oxygen diffusion into the bulk sample.

Conclusions:

Applications for high-T_C superconductors have been reviewed, and the primary obstacle toward viability of wires is the low critical current density. Several processing techniques for bulk and composite wire have been presented, and may applied generally to the expanding class of high-T_C superconducting materials. A wide variety of properties have been measured for the $YBa_2Cu_2O_{7-x}$ system. Critical current densities range from 650 to17,000 A/cm^2 depending on the fabrication technique. High frequency properties of extruded wire have also been measured and low resistances have been observed in the MHz range. Processing effects on microstructure is a subject of continuing research with the aim of improving electric and mechanical properties. Composite structures are necessary for many reasons including quench protection, thermal energy removal, and improved mechanical strength.

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Table 1

Thermal Expansion Coefficients for Selected Substrate Materials

Material	Mean Thermal Expansion Coefficient (°C $^{-1}$) x 10^6	Temperature Range (°C)	Reference
$SrTiO_3$	11.1	30-900	[27]
Zirconia (Y Stabilized)	10.3	0-1000	[28]
MgO	13.0	0-1000	[28]
Al_2O_3	8.8	0-1000	[28]
SiO_2 glass	0.5	0-1000	[28]
Cu	20.1	20-900	[29]
Ag	23.1	20-900	[29]
Au	16.8	20-900	[29]

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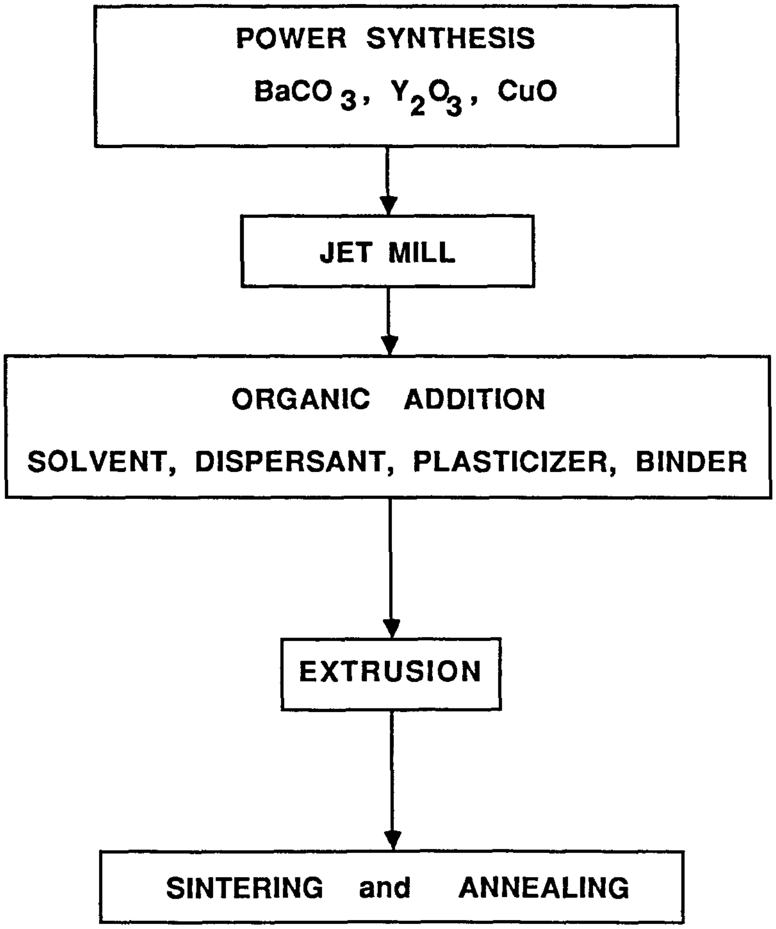
POWER SYNTHESIS
$BaCO_3$, Y_2O_3, CuO
JET MILL
ORGANIC ADDITION
SOLVENT, DISPERSANT, PLASTICIZER, BINDER
EXTRUSION
SINTERING and ANNEALING

GOOD