Thermochimica Acta, 174 (1991) 239–251
Elsevier Science Publishers B.V., Amsterdam

FORMING METHODS FOR HIGH T_c SUPERCONDUCTORS

G.S. GRADER and D.W. JOHNSON, Jr.
AT&T Bell Laboratories, Murray Hill, NJ 07974 (U.S.A.)

(Received 29 January 1990)

ABSTRACT

This paper summarizes current research on a variety of ceramic forming techniques which have been applied to bulk, high T_c superconductors. The processing methods can be divided into two major classes depending on whether or not the melting point in the material is exceeded. Growth from melts can result with a directional grain growth which improves the links between the grains. However, even a short duration above the melting point can improve the grain-to-grain coupling, and usually result in improved transport properties. In what follows we outline the shapes produced by each forming technique as well as the resulting material properties.

INTRODUCTION

Forming of high T_c superconductors is a particular challenge because the brittle nature of these ceramic materials precludes the swaging and wire drawing processes utilized for metallic low temperature superconductors. Fabrication of these high T_c materials in thin film form has been relatively successful in that materials having high T_c and high J_c values have been demonstrated. However, these methods are slow and demand expensive substrates. Such processes have promise for applications such as interconnection technology and sensor devices but are not useful in the preparation of bulk superconductors which may have applications such as high field magnets, power transmission and power storage.

For such bulk applications it is likely that either the superconductor is shaped prior to sintering or that it can be formed in sufficiently narrow diameter filaments that after sintering they can be elastically deformed into coils, etc., without fracture. In either case, forming plays a crucial role in the successful utilization of these exciting materials.

Forming methods for ceramic materials are well developed and, in some cases, highly specialized fields. Many of these methods have been shown to be adaptable to high T_c ceramic superconductors, and others not commonly used have been developed for these superconductors.

0040-6031/91/$03.50

The oldest ceramic forming methods utilize the plastic behavior of clay–water mixtures. These have been formed by shaping the plastic mass, slip casting low viscosity slurries in molds for complex shapes or extrusion of the plastic mass for shapes of continuous cross section such as tubes. For high technology ceramics, these methods are again used, but the addition of organic binders to high purity ceramic powders is required to impart the plastic behavior. For superconductors, extrusion of rods has been successfully demonstrated and slip casting of shapes is also possible although the use of water as the liquid phase is not optimal for all superconductors because of hydrolysis and other reactions. This drawback does not necessarily preclude the use of water, since the phase can again form during the subsequent sintering operation.

Another typical ceramic forming method is dry pressing of powders. A straightforward process of uniaxially or isostatically pressing the powder into a desired shape, it can utilize small fractions of organic binder to enhance the strength of the unsintered parts. Unlike extrusion, this method can not be used to fabricate continuous long conductor shapes.

Tape casting of a viscous slurry containing ceramic particles in a binder/organic solvent is another fabrication method which has been adapted to forming sheets of high T_c superconductor. An even more viscous paste has been utilized in screen printing of superconductor thick film patterns on substrates.

Unlike metal fabrication, melting of ceramic materials is not generally used since they tend to be refractory and have large volume changes on solidification. The volume changes combined with the brittle nature of ceramics in the solid state causes cracking during the solidification process. Large grains can grow, which further degrade strength. However, as will be described below, methods for melting or partially melting superconducting oxides have been very successful in attaining high critical current densities in bulk materials.

Finally, oxidation of metals is another synthesis and forming route seldom used in ceramics because the volume change from metal to oxide often results in fractured or spoiled bodies. Again for oxide superconductors, such methods have been used successfully to attain higher critical currents.

SUPERCONDUCTOR FORMING TECHNIQUES

This section summarizes a variety of ceramic forming techniques that have been applied to high T_c materials. For each forming technique we outline the shapes produced by it as well as the resulting material properties. In preparing this survey we have attempted to include a wide and up-to-date literature survey. However, owing to the immense amount of literature in

this young field, our survey is no doubt imperfect, and we apologize to those authors whose relevant work may have been omitted.

The forming methods can be divided into two broad classes: in one class all the processing steps are kept below the melting point of the material, while in the other class the melting point is exceeded for various durations depending on the technique. The two classes are connected in that a sample may be initially fabricated by the first class, to obtain a rigid body or powder, and then reheated under conditions of the second class, where melting is always present. Examples of this combination can be found in press forging and melt textured growth (MTG).

When forming various shapes of ceramic materials, it is common to mix the powder with an organic binder system which provides the necessary rigidity to the body, prior to its sintering. When a binder is added it is crucial to determine its burn-out rate, which is commonly done using thermogravimetry. If this process is too rapid, the evolved gas may induce cracks and fractures in the body, thereby degrading its final mechanical (and electrical) properties. During the binder burn-out it is also important to provide sufficient oxygen to prevent the formation of carbon residues in the sample.

Aside from fabricating shapes which may have utility, one of the main practical objectives in this field (and one for which the potential payback is the greatest) is achieving large critical currents, J_c in the samples. Another related objective is that J_c will not be affected adversely by the presence of magnetic fields, or by the self induced field. These two criteria (the J_c and its magnetic field dependence) form the most common basis for comparison of similar samples prepared by different techniques. So far the best results for bulk samples have been obtained by the second class of forming techniques, where the conditions are such that a liquid phase is present during the sintering stage. The conventional preparative methods give rise to polycrystalline, non-oriented samples which have both a low J_c (100–1000 A cm^{-2}) and a severe field dependence (i.e. J_c falls by $> 90\%$ at a magnetic field of 100 Oe). The unconventional methods involving a liquid phase give rise to a highly textured microstructure with $J_c > 10^4$ A cm^{-2} at zero field (ZF), which drops by $\sim 50\%$ at a magnetic field of 1 Torr (10^4 Oe). The remainder of this section will discuss some of the more common fabrication methods along with their achievements to date.

Dry pressing

Dry pressing is the simplest and most widely used forming technique in ceramic processing. Typically, component powders such as oxides or carbonates are weighed, mixed and then pre-reacted (calcined) to enhance the chemical homogenity of components, to induce the formation of desired phases and to reduce shrinkage which accompanies the final consolidation

(sintering) step. When high green (unsintered) strengths are required, an organic binder (e.g. PVA, acrylic resins, etc.) is added to the powder (1–5% by weight), and the powder is pressed in the 100–200 MPa range. When a binder is employed, a non-aqueous solvent is preferred (i.e. alcohols or MEK), because water adversely affects the Y–Ba–Cu–O system [1,2]. Since it is mainly the barium that is susceptible to H_2O and CO_2 attack, the Tl–Ba–Ca–Cu–O system is also expected to be water sensitive, although to our knowledge, no reports on this subject have been made. In addition, one should check the chemical make-up of the binder to ensure that it does not contain impurity cations such as Na, Ca, Fe, etc., which are commonly found in commercially available binders. In dry pressing or isostatic pressing, binders are not always necessary to fabricate simple shapes such as disks, rods, bars and tubes. For Y–Ba–Cu–O the as-pressed density is about 50% of theoretical, and after sintering the final density of these products can be close to theoretical (~ 97%) depending on the sintering conditions. For some cases liquid phase can be induced by rapid heating to the 900–975 °C range [3]. This liquid, resulting from the partial melting of CuO, enhances the sintering rate and final density of the sample.

In general, the transport properties of dry pressed samples are relatively poor. This is caused by the weak-link coupling of the non-oriented grains in the sample or microcracks between grains. Due to the anisotropic size change of the 1-2-3 unit cell during oxidation, the random orientation between grains can induce cracking at grain boundaries [4,5]. The cracks reduce the J_c through the sample, while the weak links are responsible for the large reduction of J_c in the presence of magnetic fields.

In the bismuth based superconductors a phenomenon called reterograde densification (expansion of the body during the sintering step) has been observed [6,7]. Recently reported work on the Bi–Sr–Ca–Cu–O system [8] shows $J_c > 10^3$ A cm^{-2} at 77 K with a T_c of ~ 95 K for the $Bi_2Sr_2CaCu_2O_{8+\delta}$ (2212) composition. The authors also report for the first time macroscopic persistent currents in toroids of the bismuth based system [9]. In other reports on the bulk Bi–Sr–Ca–Ca–O system, the typical J_c at 77 K is 10–100 A cm^{-2}. The method by which such improved results were obtained is to subject the sample to a partial melting at temperatures above 900 °C.

Work on the Tl–Ba–Ca–Cu–O system is plagued by the volatility of the thallium at the synthesis temperatures. The loss of thallium can be slowed by using sealed quartz containers [10]. However, the thallium reacts readily with the quartz, which can cause devitrification and fracture of the quartz ampules during cooling [11]. Another approach has been to use gold crucibles or foils to contain the reactants [12]. Our experiments on this system always showed severe staining on both sides of thick gold foils (> 20 mil), indicating that even gold, although better than quartz, is not an ideal buffer material. Cook et al. [13] have recently reported that sealed MgO crucibles provided a good containment of the reaction. The best reported

transport current in a bulk thallium sample [14] has been $> 5 \times 10^3$ A cm^{-2} at zero magnetic field. The sample was obtained by sectioning a partially melted disk. Typical results with thallium based superconductors have been around 100 A cm^{-2} at 77 K and zero magnetic field.

Press forging

Press forging refers to heating a ceramic sample under a uniaxial pressure. The main incentive to this scheme is to increase the grain orientation in a particular direction. For example, oriented $Bi_4Ti_3O_{12}$ ceramics have been made by this route [15]. The copper based high T_c grains are all anisotropic, being shorter along the *c*-axis. This anisotropy results from a slower grain-growth rate along the *c* axis than along the *a* or *b* axis. Therefore, the platelet-like grains of the high T_c materials should be readily aligned under a uniaxial pressure.

The first reported forging experiments by Robinson et al. [16] were carried out at 975 °C for 1 h, at a constant force of 600 N. Their starting material was a 12 mm disk compacted at 76 MPa. Based on the peak intensity of the 006/200 lines relative to a randomly oriented sample, the enhanced orientation observed by Robinson et al. was 7/1. A large improvement was obtained by placing a pre-sintered disk (25 mm diameter) between zirconia felt and gold foil [17]. The gold provided a smooth flow surface and the felt prevented sticking to the alumina rams. The experiments were carried out at ~ 1000 °C where a liquid phase was present under a pressure of 26 MPa. The orientation was > 70/1, with a $J_c > 3000$ A cm^{-2} at zero field in a thin oxidized layer of the sample. It was the liquid formed by partial melting which provided the improved flow characteristic in this experiment. More recent work by Takenada et al. [18] under similar conditions (~ 10 MPa, 1000 °C, with platinum spacers), also shows an enhanced orientation similar to that of ref. 17. The reported J_c at zero field was 110 A cm^{-2}.

Screen printing

Screen printing of the high T_c superconductors falls in the realm of polycrystalline thick films. The process requires a thick slurry of suspended superconducting particles in a volatile solvent (i.e. MEK or alcohols), often with an organic binder. The slurry is forced through a masked screen with an elastomer bar. The resulting films are typically 10–100 μm thick. The difficulties encountered with this technique are due both to the inherent polycrystalline nature of the film, and to its interaction with the substrate on which the film is printed. Very few reports of orientation in the films are available. Tabuchi and Utsumi [19] report seeing orientation only with a 10 μm thick film which was fired at 980 °C for 6 min on yttria stabilized

zirconia (YSZ) substrate. The preferred *c*-axis orientation is attributed to an interfacial reaction with the substrate in which $BaZrO_3$ is generated [20]. Nevertheless, the transport properties of their film were $R = 0$ at 89 K and $J_c(77\ K) = 7–30\ A\ cm^{-2}$. In another report on an oriented screen printed film over a glass buffer layer on an Al_2O_3 substrate [21], a $J_c(77\ K) = 100\ A\ cm^{-2}$ and an R = 0 at 82 K were reported.

In general, however, interaction with the substrate is very severe where barium is the most reactive moiety. An approach to reduce this interaction has been either to place a buffer layer between the film and the substrate, or to find an appropriate substrate. For example, Kitagawa et al. [22] claim that a ZrO_2 buffer layer on a silicon substrate protected the YBCO film from interaction with the silicon. The best critical current results, however, have been obtained by using Y_2BaCuO_5 (211 phase) as a substrate. Yoshira et al. [23] A have obtained a $J_c(77\ K) = 3000\ A\ cm^{-2}$ with a $T_c(R = 0) = 86$ K. In another work [24] the films were found to have excellent adhesion to the 211 phase.

Spray Pyrolysis and Dip Coating

As in screen printing, the end product of spray pyrolysis and dip coating is a thick polycrystalline film. The advantage over screen printing is that any shape can be coated, thus rendering the techniques useful in magnetic shielding applications. However, the problems of substrate interactions and non-texturing of the films are present in these techniques—just as in screen printing.

A commonly used precursor in spray pyrolysis is an aqueous solution of the metal nitrates, which is sprayed on a hot substrate [25]. A substrate temperature of 550 °C suffices to decompose the nitrates, while a heat treatment in the range 900–950 °C provides the predominantly 1-2-3 phase with a $T_c \sim 90$ K. Barboux et al. [26] have sprayed and dip-coated nitrate precursors of the bismuth and thallium based compounds on various substrates. By firing for a short duration, the evaporation losses of Bi and Tl were minimized, and $T_c(R = 0)$ values were 75 K and 95 K respectively. The critical currents are still low: $J_c(77\ K) \simeq 50\ A\ cm^{-2}$ for the thallium film. Nakada et al. [27] have dip coated MgO substrates with 1-2-3 film. Their high temperature treatment was at 1000 °C, resulting in a film having a $T_c(R = 0) = 80$ K and a $J_c(77\ K) = 70\ A\ cm^{-2}$.

Tape casting

Tape casting is used to generate flexible unfired ceramic powder/binder sheets that can be cut or shaped as desired, and fired to yield a final body. The process first requires the preparation of a viscous suspension of the superconducting powder in a binder/solvent system. The suspension is then

poured into a reservoir having a horizontal slit at the bottom of one end (called a doctor blade). The reservoir is then moved relative to the flat surface under it, leaving a thin layer of the slurry behind. Once the solvent dries, the tape can be peeled off the carrier surface for further processing. A detailed description of tape casting has been outlined by Johnson et al. [28]. Tape casting can provide sheets whose thickness is 25–1000 μm; the lower end overlapping the upper end of thick film processes. Unlike screen printing, the inherent problem of substrate interaction with the thick film is absent here. This probably explains the better transport properties obtained with thin tapes as compared with thick films [29–31]. A T_c of 92 K and J_c(77 K) of 10^3 A cm^{-2} have been observed for tape about 100–150 μm thick. Still, the main difficulty with tapes is the inability to induce a high degree of orientation in the final product. It has been reported that addition of silver (10 wt.%), to the 1-2-3 matrix resulted in an improved T_c (~ 82 K) and large oriented grains [32,33]. However, the J_c was still relatively low at ~ 80 A cm^{-2}. This issue has been tackled in two ways [34]. One method relies on the magnetic moment of the 1-2-3 crystal which can align in large magnetic fields. Yet another approach is to rely on the anisotropic nature of the high T_c crystals, which tend to settle in the slurry with the flat side along the tape direction. These grains also have a tendency to align when subjected to the shearing forces in the laminar flow under the doctor blade. The main obstacle in the last approach is that the grains are usually agglomerated, and therefore the anisotropy is not present at the size scale of the agglomerates. Neither of these alignment methods led to tapes with enhanced J_c.

Extrusion

Extrusion is a classical process for wire fabrication. As in tape casting the process requires the mixing of the superconducting powder into a binder/solvent system. The viscosity of this mixture must be higher than that required in tape casting, and the binder must set quickly in order to retain the wire shape after the extrusion. In the green state, the wire can be shaped into a coil by extruding onto a rotating madrel [35,36]. A method which circumvents the use of a solvent employs a thermoplastic polymer [37,38] (i.e. polyethylene). With this method the powder is first mixed at a temperature above the melting point of the polymer, followed by extrusion at high temperature. The temperature drop at the exit of the die provides for the rigidity of the wire. Typical wire diameters made by extrusion are 200–1000 μm, and the critical current is in the 500 A cm^{-2} range [35]. When using a long-chain linear polymer, it is possible to draw the wire faster than its extrusion rate, thereby reducing its diameter much as in fiber drawing. Our best transport results were $J_c > 2000$ A cm^{-2} at zero field on an ~ 200 μm wire [38]. In a related process called suspension spinning, Gotto and Kada [39,40] have generated wires by extruding 1-2-3 powders mixed with PVA

into a precipitating medium. The wire diameters ranged from 10–200 μm with a $J_c = 680$ A cm^{-2} and a tensile strength of 37 Mpa (for a 200 μm wire).

It has been recently reported that the critical current in wires varies inversely with wire diameter [38,41]. This effect can be attributed to the magnetic field, generated by the flowing current (the self field effect). The magnetic field outside the wire varies inversely with the radius ($B = i/2\pi r$), however, J_c varies inversely as the square of the radius, ($J_c = i/\pi r^2$). Substituting for i yields $J_c \propto B/r$, which correlates well with the observed data.

One of the motivations for the extrusion work (especially with a long-chain linear polymer) is to impart grain orientation via the shearing forces on the anisotropic platelet-like grains. The enhanced orientation would result in a much smaller reduction of J_c with magnetic fields. To date, however, only a minor enchancement of orientation has been observed via extrusion, mainly because the aggregation of the grains reduces their effective anisotropy. The aggregation also prevents a wire/polymer composite from being drawn to a small diameter.

The highest reported transport current in polycrystalline wires has been measured in thin filaments obtained by packing a powder into a metal tube (Ag or Cu) followed by wire drawing the tube to a small thickness [42–44]. This is followed by the appropriate heat treatments. In this process both a reduction in wire diameter and enhanced grain orientation are responsible for the improved properties.

Plasma spraying

Plasma spraying has been shown in the past to produce high purity, finely divided ceramic powders [45]. The application of this technique to a coating operation is attractive for several reasons: (1) highly uniform films 10–200 μm thick can be readily made [46–48], and (2) the as-deposited films are denser than the corresponding films made from organic or nitrate precursors by dipping or spraying. Therefore, the sintering time is expected to be shorter than the corresponding time for a porous film resulting from the decomposition of the organic or nitrate precursured film. This technique, however is also hindered by substrate interaction and difficulties in obtaining oriented films.

Typical zero resistance temperatures are 80–90 K. However, not many reports of J_c in plasma sprayed films have been made. The best results by Tachikawa et al. [47] are a J_c(77 K) of 690 A cm^{-2} at zero magnetic field.

Metal oxidation

The metal melt oxidation (MMO) process (also referred to as liquid–gas solidification (LGS) process) is potentially applicable to any superconductor

system. It has been demonstrated on the Yb–Ba–Cu–O system as well as bismuth and thallium based materials [49,51]. The process involves first melting the respective pure metals to give a homogeneous liquid under a neutral or reducing atmosphere. A substrate is then dipped into the molten metal and pulled out, coating the surface with a liquid film. Following the coating, the substrate is exposed to oxygen, and the film is oxidized at the melt temperature. It has been found that the grain growth starts at the film/substrate interface, and thus the film morphology is influenced by the choice of substrate material and its orientation [52].

This technique is naturally applied to thin/thick film applications. Experiments with 1-2-3 on $SrTiO_3$ substrates have yielded a 3 μm thick film with a $J_c = 1.7 \times 10^4$ A cm^{-2} [49]. Work on the thallium based materials [52] has also yielded highly textured films; however, due to thallium vaporization, some secondary phase occurred and the film exhibited a creep phenomena reported earlier in the thallium based material [53].

A similar approach has been taken by melt spinning metal ribbons of the metallic precursors [54,55]. A noble metal (i.e. Ag or Au) may also be added to the original mixture. The molten mixture is quenched onto a rotating copper wheel in an argon atmosphere. The resulting ribbons are typically several millimeters long, 20 μm thick, and about 70% amorphous. The ribbons are subsequently oxidized by heating in air to 800–900 °C at 10 °C min^{-1}, soaking at the higher temperature for 3–10 h, then furnace cooling to room temperature [55]. The resulting microstructure is not textured and the transport properties are typical of normally processed bulk material (~ 200–300 A cm^{-2} at 77 K in zero field).

Clearly there is a vast difference between the microstructure and transport properties of the samples produced by the MMO and melt spinning processes. The reason for this is that in the MMO process the crystal nucleation and growth at the substrate interface occur at a temperature where the superconducting phase is thermodynamically stable. In addition, the cation and oxygen transport to the growing crystal occurs through the metallic liquid phase. The growth process is therefore much faster than transport through a solidified ribbon of the melt spinning process. More importantly, in the spinning process the as-spun ribbons are partially crystallized (30%). These crystals (which are not superconducting) grow during the heating period, thus the free energy change in forming the superconducting phase is lower (since other crystals must decompose to provide the cations). Also, the final morphology of the ribbon is likely to be determined by the original orientation of the crysals (which are probably randomly distributed), probably giving a non-oriented grain growth.

Growth from oxide melts

Ceramic processing methods are seldom designed to invoke liquid phases (other than very small amounts of liquid to enhance sintering kinetics)

because the volume changes on solidification can lead to cracking and the large grains produced are generally undesirable. This is especially so in the case of incongruently melting compounds since the melting leads to segregation of the components. Nevertheless, a few cases of enhanced crystal growth by cooling incongruent melts have been demonstrated [56,57]. For the Y–Ba–Cu–O superconductors Jin et al, [58,59] developed a technique utilizing melts of this incongruently melting compound which have resulted in the highest reported J_c values for bulk samples.

In this technique, termed "melt textured growth", a presintered sample is heated above the incongruent melting point. The specimen is then cooled in the presence of a temperature gradient. Since all the cuprate-based superconducting grains are naturally anisotropic in shape, the grains grow faster in the direction of the gradient—which happens to be the conduction direction in these layered materials (the a–b plane). Specifically, the samples were heated in the 1050–1200 °C range and then cooled at a gradient of 50 °C cm^{-1} to 900 °C. These melt textured samples were essentially 100% dense, and had grain sizes of length 100–3000 μm and width 20–50 μm. The resulting transport properties $J_c = 1.7 \times 10^4$ A cm^{-2} (at 77 K and zero field), and $J_c = 4000$ A cm^{-2} at $H = 1$ Torr. Recently Salama et al. [60] reported a $J_c(77\ K) = 7.5 \times 10^4$ A cm^{-2} in zero field, and 3.7×10^4 A cm^{-2} at 0.6 Torr, in a melt textured sample grown without a temperature gradient.

Pedestal growth [61,62] and float zoning [63] techniques have also been attempted for the production of superconducting wires. These techniques have been largely unsuccessful for the Y–Ba–Cu–O system (presumably due to the bubbling of oxygen); however, progress has been made in the Bi–Sr–Ca–Cu–O system. The laser-heated pedestal growth method (LHPG) for high T_c material is a continuation of earlier studies on growth of oxides such as $BaTiO_3$ [62]. This technique consists of heating the top of a rod with CO_2 lasers, inserting a seed into the molten puddle, followed by pulling the seed and the growing crystal upward. The loss of liquid to the growing fiber is compensated by raising the feed rod into the laser beam. One of the limitations of this technique is that the fiber cannot be pulled downward. Since the heat in this system is transferred upward via the surrounding gas, the net effect is to lower the temperature gradient in the growing crystals. Fibers with a 0.25–1.00 mm diameter have been grown in a variety of atmospheres. Dense and highly oriented samples were obtained at a slow growth speed of 4.8 mm h^{-1}. The shape of the resistivity plot for the samples shows the presence of two superconducting phases. However, in the X-ray pattern of the fiber (X-ray plane normal to fiber direction), only the lower temperature phase (2212) is observed. Critical current measurements using the pulsed method on these specimens indicate a value in excess of 6×10^4 A cm^{-2} (at 68 K).

In the float zoning work [63], four CO_2 laser beams are focused on a 0.36 cm diameter rod of the superconductor. The lower and upper sections of the

rod are rotated in opposite directions (10–50 rpm), while the rod is pulled down at a rate of 0.10 cm h^{-1}. Unlike the LHPG method, this technique allows both upward and downward pulling. It has been found that much better results were obtained when pulling downward, consistent with the larger temperature gradient in that direction. The resulting crystal sizes are $3 \times 1.2 \times 0.3$ mm. Although there is a high degree of orientation, the transport properties of the samples are very similar to bulk prepared materials. A maximum of 140 A cm^{-2} is reported for one of the samples.

SUMMARY

The field of high T_c superconductor processing is young, less than three years old. Rapid progress has been made in applying existing ceramic forming methods to these new and difficult materials. Furthermore, new forming processes have been invented to optimize the properties.

Yet the technology is by no means optimal. The challenge in processing of bulk high T_c superconductors is to form these materials into shapes appropriate for potential applications, while allowing high J_c preferably in high magnetic fields. Thin film work has demonstrated that the high J_c properties are possible, and for this reason those applications which can utilize thin films may come to fruition earliest. For bulk processing, great strides have been made in measuring the $\leqslant 10^3$ A cm^{-2} values seen in randomly oriented polycrystalline materials using melt processing methods such as melt textured growth or metal melt oxidation. Nevertheless, limited progress has been made in applying these methods to fabricating long wire-like or filamentary structures which would be useful in most applications involving bulk high T_c superconductors.

The understanding that critical current is proportional to inverse radius of filaments offers some opportunity in fabrication cabled wire for power transmission, if forming methods can be developed to make very long lengths of filament. Small diameter filaments could be cabled without breakage because of the elasticity of the material. Such a multifilamentary cable should not degrade J_c since the self induced magnetic fields will largely cancel within the cross section. On the other hand, such cable could not be used in magnet applications because of high field contributions from the winding. Such applications await a technology for forming wire with high J_c and little degradation of J_c in magnetic fields.

REFERENCES

1 M.F. Yan, R.L. Barns, H.M. O'Bryan, P.K. Gallagher, R.C. Sherwood and S. Jin, Appl. Phys. Lett., 51 (1987) 532; K. Komori, H. Kozuka and S. Sakka, J. Mat. Sci., 24 (1989) 1889.

2 P.K. Gallagher, G.S. Grader and H.M. O'Bryan, Mater. Res. Bull., 23 (1988) 1491.
3 H.M. O'Bryan, personal communication.
4 H.M. O'Bryan and P.K. Gallagher, Adv. Ceram. Mater., 2 (1987) 640.
5 S. Nakahara, G.H. Fisanick, M.F. Yan, R.B. VanDover and T. Boon, J. Crystal Growth, 85 (1987) 639; Appl. Phys. Lett., 53 (1988) 2105.
6 D.W. Johnson, Jr., and W.W. Rhodes, J. Am. Ceram. Soc., 72 (1989) 2346.
7 N. McN. Alford, T.W. Button, J.D. Brichall, W.J. Clegg and K. Kendall, 1989 American Ceramics Society Annual Meeting, 23–27 April, Indianapolis, IN.
8 K. Imai and H. Matsuba, Workshop on High T_c Superconductivity, 23–25 May 1989, Huntsville.
9 H. Matsuba, A. Yahara and K. Imai, submitted.
10 S.S.P. Parkin, V.Y. Lee, E.M. Engler, A.I. Nazzal, T.C. Huang, G. Gorman, R. Savoy and R. Beyers, Phys. Rev. Lett., 60 (1988) 2539.
11 G.S. Grader, unpublished results.
12 C.C. Torardi, M.A. Subramanian, J.C. Calubrese, J. Gopalakrishnan, K.J. Morrissey, T.R. Askew, R.B. Flippen, U. Chowdhry and A.W. Sleight, Science, 240 (1988) 631.
13 L.P. Cook, D. Blackburn, C.K. Chiang, W. Wong-Ng and L. Swartzendruber, 1989 American Ceramics Society Annual Meeting, April 23–27, Indianapolis, IN.
14 E.L. Venturini, J.F. Kwak, D.S. Ginley, B. Morrosin and R.J. Baughman, Progress in High T_c Superconductivity, Vol. 17, Work Scientific Publishers, NJ, 1988, pp. 169–189.
15 T. Takenaka and K. Sakata, Jpn. J. Appl. Phys., 19 (1980) 31.
16 Q. Robinson, P. Georgopoulos, D. Johnson, H.O. Marcy, C.R. Kannewurf, S.J. Hwu, T.J. Marks, K.R. Poeppelmeier, S.N. Song and J.B. Ketterson, Adv. Ceram. Mater, 2 (1987) 380.
17 G.S. Grader, H.M. O'Bryan and W.W. Rhodes, Appl. Phys. Lett., 52 (1988) 1831.
18 T. Takenaka, H. Noda, A. Yoneda and K. Sakata, Jpn. J. Appl. Phys. Lett., 27 (1988) L1209.
19 J. Tabuchi and K. Utsumi, Appl. Phys. Lett., 53 (1988) 606.
20 J. Tabuchi, A. Ochi and K. Utsumi, Jpn. J. Ceram. Soc., 96 (1988) 450.
21 D. Bhattacharya, C.K. Maiti, P. Pramanik, T.K. Dey, S.K. Ghatak and K.L. Chopra, Thin Solid Films, 164 (1988) 115.
22 T. Kitagawa, S. Shibata, H. Okazaki, T. Kimura and Y. Enomoto, Jpn. J. Appl. Phys. Lett., 27 (1988) L1113.
23 K. Yoshiara, K. Kagata, S. Yokoyama, T. Hiroki, H. Higuma, T. Yamazaki and K. Nakahigashi, Jpn. J. Appl. Phys. Lett., 27 (1988) L1492.
24 W.N. Wang, H.B. Lu, W.J. Lin and P.C. Yao, Jpn. J. Appl. Phys. Lett., 27 (1988) L1265.
25 L.N. Yannopoulos, H. Lessure, Y. Xu, S. Simizu and S.G. Sankar, World Congress on Superconductivity, Houston, TX, 20–24 February 1988.
26 P. Barboux, J.M. Tarascon, F. Shokoohi, B.J. Wilkens and C.L. Schwartz, J. Appl. Phys., 64 (1988) 6382.
27 T. Nakada, M. Kazusawa, A. Kunioka and T. Fujimori, Jpn. J. Appl. Phys. Lett., 27 (1988) L873.
28 D.W. Johnson, Jr., et al., Adv. Ceram. Mater, 3 (1987) 364.
29 D.W. Johnson and G.S. Grader, J. Am. Ceram. Soc., 71 (1988) 291.
30 M. Ishii, M. Mutsuda, M. Takata, T. Yamashita and K. Tsukamoto, Jpn. J. Appl. Phys. Lett., 27 (1988) L1420.
31 G.J.J. Beckers and R.A. Terpstra, J. Mater. Sci. Lett., 7 (1988) 703.
32 J.P. Singh, U. Balachandran, D. Shi, J.K. Degener and R.B. Poeppel, Mater. Lett., 7 (1988) 72.
33 J.P. Singh, D. Shi and D.W. Capone, Appl. Phys. Lett., 53 (1988) 237.
34 D.W. Johnson, Jr., W.W. Rhodes, G.S. Grader and E.M. Gxorgy, Proc. MRS Meeting, Tokyo, 31 May–June 3, 1988.

35 M.T. Lanagan, R.B. Poeppel, J.P. Singh, D.I. Dos Santos, J.K. Lumpp. U. Belochandron, J.T. Dusek and K.C. Guretta, Proc. Rare Earth Res. Conf., Interlaken, 12–16 September 1988.
36 R.B. Poeppel, S.E. Porris, C.A. Youngdahl, J.P. Singh, M.T. Lanagan, U. Balachandram, J.T. Dusek and K.C. Goretta, J. Met. 41 (1989) 11.
37 A. Pearson and A. Crestwood, U.S. Patent No. 4071594, 1978.
38 G.S. Grader, H.M. O'Bryan, W.W. Rhodes, D.W. Johnson, Jr., P.K. Gallagher, C. Gieniewski, L. Shepherd and L. Johnson, 1989 American Ceramics Society Annual Meeting, 23–27 April, Indianapolis, IN.
39 T. Gotto and M. Kada, J. Mater. Res., 3 (1988) 1292.
40 T. Goto, Jpn. J. Appl. Phys. Lett., 27 (1988) L680.
41 G. Lu, W. Coblenz and M. Cima, 1989 American Cereramics Society Annual Meeting, 23–27 April, Indianapolis, IN.
42 H. Sekine, K. Inoue, H. Maeda, K. Namata, K. Mori and H. Yamamoto, Appl. Phys. Lett., 52 (1988) 2261.
43 M. Okada, A. Okayama, T. Matsumoto, Y. Morii and S. Funahashi, Jpn. J. Appl. Phys. Lett., 27 (1988) L1715.
44 S. Jin, R.C. Sherwood, R.B. VanDover, T.H. Tiefel and D.W. Johnson, Jr., Appl. Phys. Lett., 51 (1987) 293.
45 R.M. Young and E. Pfender, Plasma Chem. Plasma Process., 5 (1985) 1.
46 J.J. Cuomo, C.R. Guamnieri, S.A. Shivashankar, R.A. Roy, D.S. Yee and R. Rosenberg, Adv. Ceram Mater., 2 (1987) 422.
47 K. Tachikawa, I. Watanabe, S. Kosuge, M. Kabasawa, T. Suzuki, Y. Matsada and Y. Shinbo, Appl. Phys. Lett., 52 (1988) 1011.
48 C.R. Guarnieri, R.A. Roy, S.A. Shivashankar, J.J. Cuomo, D.S. Yee and R. Rosenberg, AIP Conf. Proc. (U.S.A.), 1988, No. 165, p. 204–10.
49 H.S. Chen, S.H. Liou, A.R. Kortan and L.C. Kimerling, Appl. Phys. Lett., 53 (1988) 705.
50 C.H. Chen, D.J. Werder, S.H. Liou, H.S. Chen and M. Hong, Phys. Rev. B, Rapid Commun, 37 (1988) 9834.
51 H.S. Chen, E.M. Gyorgy, L.C. Kimerling, A.R. Kortan and F.A. Thiel, Mod. Phys. Lett. B, 3 (1989) 975.
52 C.H. Chen, H.S. Chen and H.S. Liou, Appl. Phys. Lett., 53 (1988) 2339.
53 G.S. Grader, E.M. Gyorgy, L.G. van Uitert, W.H. Grodkiewica, T.R. Kyle and M. Eibschutz, Appl. Phys. Lett., 53 (1988) 319.
54 G.J. Yurek, J.B. van der Sandle, D.A. Rudman, and Y.M. Chiang, J. Met., 1 (1988) 16.
55 T. Kogure, R. Kintra, and J.B. van der Sandle, Physica C, 156 (1988) 35.
56 J.S. Haggerty, W.P. Menashi and J.F. Wenckus, U.S. Patent 3944640 (March 1976).
57 Y. Fujiki, J. Jpn. Ceram. Soc. (Yogyo-Kyokai Shi), 91 (1983) 189.
58 S. Jin, T.H. Tiefel, R.C. Sherwood, R.B. VanDover, M.E. Davis, G.W. Kammlott and R.A. Fastnacht, Phys. Rev. B, 37 (1988) 7850.
59 S. Jin, T.H. Tiefel, R.C. Sherwood, M.E. Davis, G.W. Kammlott, R.A. Fastnacht and H.D. Keith, Appl. Phys. Lett., 52 (1988) 2074.
60 K. Salama, V. Selvamanickam, L. Gao, and K. Sun, Appl. Phys. Lett., 54 (1989) 2352.
61 R.S. Fiegelson, P. Gazit, D.K. Furk and T.H. Geballe, Science, 240 (1988) 1642.
62 R.S. Feigelson, J. Crystal Growth, 79 (1986) 669.
63 H.D. Brody, J.S. Haggerty, M.J. Cima, M.C. Flemings, R.L. Barns, E.M. Gyorgy, D.W. Johnson, W.W. Rhodes, W.A. Sunder and R.A. Laudise, J. Crystal Growth, 96 (1989) 225.