ABSTRACT

"Friction free" bearings at 77 k or higher are possible using the high-Tc copper oxide ceramic superconductors (1) (2). The conventional method for making such bearings is to use a sintered ceramic monolith. This puts great restraints on size, shape, and post-forming machining. The material is hard and abrasive. It's possible to grind up ceramic superconductors and suspend the granules in a suitable matrix. Mechanical properties improve and are largely dependent on the binder. The Meissner effect is confined to individual grains containing vortices (3). Tracks, rails, levitation areas and bearings can be made this way with conventional plastic molding and extruding machines or by painting. The parts are easily machined. The sacrifice is in bulk electrical property.

A percolating wick feed for LN$_2$ can be used to cool remote superconductors and large areas quite effectively. A hollow spheroid or cylinder of superconductor material can be molded with the internal surfaces shielded by the Meissner effect. It might be thought of as the DC magnetic analog of the Farady cage and the inside can be called the "Meissner space."

It's selective. AC fields are transmitted with minor attenuation. Particle size and distribution have a profound effect on final magnetic and electrical characteristics.

INTRODUCTION

High-Tc superconductors are usually made of pressed ceramic, vapor-deposited or sputter-deposited films. Some have been made from solutions of the appropriate precursors (4) (5) (6). Most researchers take great pride in making the pressed ceramics as close to "theoretical density" as possible. Their desire is to produce the very best electrical and magnetic properties. However, this is not a field where conventional wisdom necessarily produces the best results. This paper will describe:

1. A technique for controlling the porosity of ceramic high-Tc superconductors to any value desired below the theoretical maximum.
2. Another technique for using granules of superconductive materials in polymers to mold nonconductive plastics that exhibit a strong Meissner effect suitable for bearings, tracks, rails, levitation areas, and DC and magnetic shielding.
3. An LN$_2$ percolating heat pipe that has been invented for cooling superconductors approximately 2.5 cm above an LN$_2$ reservoir. It can be bonded to the high-Tc superconductor for remote cooling.
4. A number of applications which are possible for bearings and magnetic shields, as long as high current density is not a requirement and the Meissner effect is of prime concern. This permits great flexibility and ease of manufacture (7) (8) (9).

POROUS HIGH Tc SUPERCONDUCTORS

All of the work in this paper uses the rare earth, barium, copper, oxygen system, particularly the Y$_1$Ba$_2$Cu$_3$O$_y$ variety. The techniques described, however, will work with any ceramic material. We have obtained good results using europium instead of yttrium in some test runs. Many rare earths are reported to work as well (10).

The precursors are carbonates or oxides of the element carefully measured for stoichiometry. They are mixed and presintered in ceramic crucibles with minimum wall contact for 5 hours in dry air to 950 C and cooled in the oven overnight.
A black klinker results. This is ground up in a mortar and pestle to form a powder that will pass about 90% through a 100-mesh sieve. So far, all is conventional. The powder is then mixed with an ash-free spectrographic grade cellulose fiber and a small amount of fluorocarbon resin powder. It is pressed at 30 tons in a 2-cm-diameter die. A cellulose reinforced pellet results.

Figure 1 is a 50X SEM photo of a compressed pellet showing the squashed fibers distributed throughout its body. The fibers are brittle and they lose their identity in the bulk of the molded part. Figure 2, at 1500X SEM, is a broken sample. The cellulose is there but it has been crushed and shattered and is hard to identify. These pellets mold nicely and are easy to handle. The cellulose, crushed or not, reinforces it significantly.

THE SECOND FIRING

The pellets are stacked so gases can flow freely around them and are placed in a silicon carbide resistance-heated tube furnace. Dry air is fed into one end at a relatively slow rate. They are gradually heated to 400°C to allow the cellulose to burn out gently. The gas is switched to O₂, or in some cases O₃, and heated over a 3-hour period to 950°C. The temperature is then increased gradually to 975°C over a period of 5 hours in flowing oxygen. The oven is then turned off and allowed to cool slowly for 12 hours in flowing oxygen or ozone.

The resulting ceramic buttons are quite porous. A 100X SEM photo (Figure 3A) shows a webwork of channels throughout the matrix. At higher magnification, tubules can be seen throughout the superconductor (Figure 3B). The ceramic grains are cemented together; however, all is electrically continuous.

The effect of PTFE and fiber loading can now be demonstrated. Since the disks are porous, they hold a charge of LN₂ after dipping in a reservoir. The levitation time above a nest of magnets increases since the disks do not warm up as rapidly as those of higher density. Figure 4 shows the levitation to be dramatically increased when 0.5% of fiber is added to the disk. Figure 5 shows that the electrical characteristics are reflected in the height of the Meissner levitation. It is enhanced by the addition of 0.5% weight of PTFE powder. The levitation height increases from 2 to 7.5mm—a considerable improvement.

FLUOROCARBON RESIN

The purpose of the fluorocarbon (Teflon) resin inclusion is twofold. First, it acts as a mold lubricant and enhances the compaction of the granules and fiber. Second, it decomposes to form a fluorocarbon gas that greatly improves the electrical and mechanical properties of the final superconductor.

The current belief in our labs is that the fluorocarbon gases reduce the melting temperature of the surface of the granules, which then acts like a solder to assure intimate contact between grains. It might also act as a crystallization flux. Note that in Figure 3B, the granules are nicely cemented together.

We measure the Meissner effect using a standard cobalt samarium magnet above a superconductor. The higher it levitates the better. The inclusion of a moderate amount of PTFE improves the properties significantly (see Figure 5).

THE ADVANTAGE OF POROSITY

Oxygen is an essential component of the high-Tc superconductors. It must diffuse through the body of the superconductor and become part of its crystal structure (2). In a high-density ceramic, this will take much longer than in one with porosity and interlaced diffusion tunnels. The result is very high-quality granular superconductors with extraordinarily strong Meissner effect. The superconductivity is not confined to the surface due to its porosity (11).

When electrical contact is made to the superconductor, the voids allow silver or gold paint to soak in deeply, making good contact to the bulk rather than just to the surface. That's advantage number one. The second advantage is that the porous superconductor acts like a liquid nitrogen (LN₂) sponge. If a pellet is dipped in LN₂, it soaks it up and carries the charge of coolant after it is removed from the coolant reservoir. It will continue to superconduct for 30 seconds to 1 minute, depending on its volume, until the LN₂ has evaporated from the piece. The third advantage is that the final fully formed superconductor is easy to grind up without crushing directly through the crystals. As a result, we can make powders of superconductors, disperse them in suitable plastic binders and make molded plastics and paints that have very high Meissner or shielding effects.

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We have used Teflon, polyester, epoxy and silicone rubber successfully for molded bulk items, sheets and paints. The objects are molded with as little binder as possible so the particle density is high. The resulting parts can be drilled, milled and turned on a machine lathe. The bulk electrical property suffers. The parts are essentially high-resistance conductors, depending on the amount of binder that is used. The Meissner effect is degraded slightly since large-diameter vortices and circulating currents cannot exist. Particle size is an important variable.

ANOMALIES

The firing of the superconductor must be carefully controlled. A general rule is that it should end up at the maximum temperature that does not cause measurable shrinkage. When the peak temperature is exceeded, a dramatic shrinkage occurs. Actual meltdown can occur if the temperature is too high. The buttons then assume the appearance of watches painted by Salvador Dali and aren't much good for anything (Figure 7). The voids are greatly reduced in size, resulting in larger crystals with poor "soldering" between crystals for reduced Meissner effect. The liquid phase will have run out and been blotted up by the ceramic supports. Higher bulk room temperature resistance results.

If the heating is performed with the superconductors stacked like bricks, one on top of the other, the second tier down has a granular glitter of microcrystals after processing. The SEM shows a most interesting crystal pattern with laminar planes visible (mica-like) running through the crystals (Figure 8). These do not have the best Meissner effect in spite of particle/particle contact being well formed.

MAGNETIC SUSCEPTIBILITY AND FLUX PENETRATION DEPTH

A fast screening test for superconductors exploits the fact that their weak field magnetic susceptibility is approximately 1/41I below Tc (12). We use two pancake coils cut from an RF choke coil. They are mounted on perforated circuit board. The superconductor under test is placed between the coils so that the three are parallel in a sandwich configuration. A standard signal is transmitted through the sample and picked up by the top coil. The two signals are displayed on a twin beam oscilloscope and preserved with an XY recorder (the X scale records temperature). When Tc is passed, the superconductor becomes opaque to the signal and transmission drops to zero. The scope signal on the output coil vanishes. Simple, easy, and fast! And superconductors are the only materials in the world that do this.

However, much to my surprise, the molded plastic granular superconductor remains fairly transparent to alternating fields and doesn't behave like the bulk superconductor on the above test. This is in spite of the fact that magnets levitate above the sample quite nicely. It turns out that their transparency is related to particle size and packing density and is never as good as the unground monolith.

The thickness of the superconductor is also an important variable (Figure 10). Penetration depth of about 8mm is shown in a stack of disks. (We continued stacking until the levitation height of the magnet stabilized.) In metallic superconductors, the super currents are located near the surface—a DC analog of the high-frequency AC skin effects in conventional conductors (13). More powerful magnets can be expected to penetrate deeper and levitate higher. This is an important consideration in bearing design.

MANUFACTURING TECHNIQUES

1. A flexible tape of silicone rubber (RTV) is easily made by mixing the granular superconductor in the RTV and doctoring it onto a carrier strip of fiberglass scrim for strength. Once cured, it can be wrapped on cylinders and spheres and bonded with additional RTV. Thickness, particle size and loading determine the depth of shielding (Figure 11A).
2. Packing—Pack the granular material in a dead soft copper tube, flattening and welding the ends after displacing the interstitial air with O2. The unit can be squashed flat and hydroformed into complicated dishes and pans. Copper is nonmagnetic so the Meissner effect is pronounced and available in deep drawn shapes, limited principally by the ductility of the container (Figure 11B).
3. Hand layups—The granular material can be mixed into epoxy or polyester resin and hand molded to surfaces for complex shapes. Fiberglass can be incorporated for strength.
4. Molding—The granular material can be mixed into thermo-setting or thermo-plastic resins and molded just like a piece of plastic. Very high production is possible in complex shapes (Figure 11C, both views). Tracks can be extruded.
5. Monoliths—Large-diameter or large-volume containers can be packed with the granular material and vacuum impregnated with suitable plastics and later machined into the final shape.
6. The porous unground ceramic can be vacuum impregnated with plastic. This creates an object that has the strength of the plastic but is electrically conducting across its bulk.

PARTICLE SIZE

In a sense, a monolithic superconductor is a one-particle body. If it is ground up, it becomes many particles of smaller and smaller size as the grinding progresses. Smallest is not necessarily best, since the diameter of a Cooper pair is on the order of approximately 20 Å (11). To make a plastic filled with superconductive particles, it is best not to grind too fine or the Cooper pair radius will be encroached. Circulating current and vortices will be adversely affected. Plastics filled with superconductive particles have been made in two ranges of particle sizes:

1. ground and passed through a 100-mesh sieve; and
2. ground and passed through a 16-mesh sieve onto a 100-mesh sieve (removing the fines).

The strongest Meissner effect is from the sample passed through the 100-mesh screen. Apparently, the particles are not yet too small. Packing will be fairly good since a full range of particle sizes passes through the finer sieve. The coarse material has had the fines removed so there is a lot of resin-filled space. The problem is similar to that of making concrete aggregates. A range of particle sizes is required to properly fill the space. The resin should only be used for a binder, not a gap filler.

PERCOLATING HEAT PIPES

A technique has been developed for cooling the plastic superconductors that dies not require them to be dipped directly in liquid nitrogen. The plastic os molded against a wick of nonwoven fabric and copper wire mesh or aluminum foam. The fabric lifts the LN$_2$ via capillary attraction to the superconductor. The mesh allows vapor to escape.

If small-diameter holes are simultaneously molded in the superconductor, they act as percolation paths. The wick-fed fluid perks up through the holes and cools the superconductor efficiently. So far, this has worked against a pressure head of about 2.5 cm. A "remote" source of LN$_2$ can therefore be used to cool large areas of superconductors (Figure 12).

WEAK LINKS

Superconductors can handle very high current density (100,000 amps per square cm) in thin films (13) or 200 to 400 amps per square cm in the granular high Tc ceramic (11). This is sufficient if one wishes to use them for high-power applications or bearings. However, the process is more complicated when used for sensors and detectors of various sorts. Their impedance is very low and difficult to work with.

The current must be limited for such applications and it is customary to use a weak link--a Dayem bridge or Josephson device to couple superconductors and reduce the current magnitude to manageable levels. The weak links must be very small (9). The technique described in this paper for controlling the porosity of the ceramic high-Tc superconductor has the possibility, if carried to its extreme, to make devices that contain a multitude of weak links in a "swiss-cheese" or sponge-like structure.

So far, we have been unable to get the circulating currents low enough to measure flux jumps or magnetic flux quanta. This is, nevertheless, an interesting possibility and we will continue to try.

SUMMARY

"WHAT’S IT GOOD FOR?" (14)

Non-conductors that exhibit the exotic magnetic properties of superconductors are very curious materials. In a sense, we can make magnetic field manipulating bodies from molded plastics. Fields can be shoved, molded and concentrated into configurations not normally attainable. For example--

- Possible uses are in levitated bearings, tracks and rails.
- Gyros come immediately to mind.
Beam shapers and plasma bottles are possible. Flux pumps and concentrators are easy to make.

Magnetic "field-free" regions inside a Meissner bottle are possible. They can be selective in that DC fields are shielded better than AC fields.

Coils and sensors can be embedded in the plastic.

A fiber/metal-mesh heat pipe can help remotely cool the superconductor. Percolation holes for LN$_2$ in the superconductor dramatically improve cooling.

The list goes on and on and the number of applications seems to go up directly with the number of engineers and scientists that are exposed to the possibilities.

There is nothing new about the idea of superconductor bearings. Levitation is as old as the Meissner-Ochsenfeld discovery. It's obvious and dramatic. Readers wishing to delve into the subject further would greatly benefit by reading Newhouse’s book (7) first. It has the best coverage of the subject I've discovered so far and has an excellent bibliography.

REFERENCES


10. Feinberg, E.O., November 15, 1988, High Tc Update, Ames Laboratory, Vol. 2, No. 22. (Note: Preprints are free to any interested party. The literature is expanding so fast that this is the best source of the most current information.)


Figure 1. 50X SEM showing cellulose reinforced ceramic after molding and before final firing in $O_2$.

Figure 2. 1500X SEM showing cellulose reinforced pellet before firing. The cellulose is brittle and doesn't show as fibers in the broken section--they are there however.
Figure 3A. 100X SEM showing pellet after second firing. The cellulose has burned out and left the pellet riddled with tunnels.

Figure 3B. 1500X SEM showing a tubule in the ceramic. Note that grains are cemented (soldered) together. The pellet resistance is about .1 ohm at room temperature.

Figure 4. A cobalt samarium magnet levitates well above the porous superconductor. The porosity contributes to fast cooldown and high thermal hysteresis—it's an LN$_2$ sponge.
Figure 5A. The addition of PTFE powder to the pellet improves the Meissner effect as measured by the height of levitation of a standard magnet (see Figure 4).

Figure 5B. The effect of cellulose loading.
Figure 6. Ground superconductor passed through a 100-mesh sieve: a) 50X SEM; b) 500X SEM; and c) 3000X SEM.
Figure 7. If superconductors are fired at too high a temperature, they droop and stick tenaciously to the ceramic support. Best results are obtained if they are fired just below this point--tricky near 1000 C.

Figure 8. When superconductors were stacked for firing, the lower one showed glitter so we took a look at a) 500X SEM, and b) 1500X SEM. Note the planes within the crystals.
Figure 9. Two pancake coils are used to measure the magnetic susceptibility of superconductors. The AC signal is applied to one and measured with the other. When a superconductor placed between them passes Tc, the AC signal output vanishes.

Figure 10. Flux penetration curve. With four disks in a stack the penetration depth for maximum levitation is about 8mm.
Figure 11. a) Silicone rubber used as a binder with a polyester non-woven fabric top and bottom gives a flexible superconductor; b) Granular superconductor compressed in copper tubing shows good Meissner effect when submerged in LN$_2$; and c) Very good superconductor bearings (above) can be machined from plastics using a high loading of particles passed through a 100-mesh sieve. Below, complex shapes can be molded.
Figure 12. a) A fabric/wire mesh heap pipe used to cool plastic molded to its top; b) Percolation holes in the top of the plastic superconductor assist greatly in cooling; c) Magnet levitates above sample about 2 cm above a reservoir of LN$_2$. 