Development of high critical current density in multifilamentary round-wire Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ by strong overdoping$^1$

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Abstract:

Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ is the only cuprate superconductor that can be made into a round-wire conductor form with a high enough critical current density $J_c$ for applications. Here we show that the $J_c(5\ \text{T}, 4.2\ \text{K})$ of such Ag-sheathed filamentary wires can be doubled to more than $1.4 \times 10^5\ \text{A/cm}^2$ by low temperature oxygenation. Careful analysis shows that the improved performance is associated with a 12 K reduction in transition temperature $T_c$ to 80 K and a significant enhancement in intergranular connectivity. In spite of the macroscopically untextured nature of the wire, overdoping is highly effective in producing high $J_c$ values.

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$^1$ To appear in Applied Physics Letters
Perhaps the most pressing wish of the large scale superconducting applications community is to develop a round wire multifilamentary conductor from a 100 K class superconductor, which could viably replace the two Nb-based materials, Nb-Ti and Nb$_3$Sn with $T_c$ of 9 and 18 K, from which virtually all superconducting applications are presently made. For more than 20 years the dream of using cuprate high temperature superconductors (HTS) with $T_c$ in the 90 to 110 K range has fueled a conviction that helium-free magnets operating at much higher temperatures are possible. The three available HTS conductors all offer the possibility to generate magnetic fields far beyond the maximum of ~22 T possible with Nb$_3$Sn, since cuprates have critical fields at 4.2 K greater than 100 T, even in the inferior direction. But the major obstacle to their use is the tendency of cuprate grain boundaries (GBs) with misorientation angle $\theta$>3-4º to have depressed $J_c$ due to local GB suppression of the carrier density and the superconducting order parameter. Thus (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ (Bi-2223) conductors have never achieved their full potential because only a partial uniaxial texture with FWHM ~10-12º can be developed, while coated conductors of YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) show much higher $J_c$ because a strong biaxial texture with FWHM<5º can be developed by epitaxial or seeded growth. But large aspect ratio tapes, ~20:1 for Bi-2223 or typically 4000:1 for YBCO, are far from optimum, because it is hard to cable flat tape conductors and tapes have large hysteretic losses in perpendicular magnetic field $H$. Since the cuprate GB problem is widely believed to be intrinsic to their small carrier density and proximity to a parent, antiferromagnetic insulating state, understanding the remarkable properties of round-wire, Ag-sheathed Bi-2212 conductor has quite general importance.

Unlike any other cuprate, Bi-2212 can attain high $J_c$ in round wires which lack long-range texture. This letter addresses the final process step that greatly enhances their $J_c$ and ties it to oxygenation treatments that overdope the Bi-2212 phase in ways that are generally not possible in Bi-2223 or YBCO.

Bi-2212 round wire is composed of a myriad of ~100-200 µm long and ~0.1-0.3 µm thick plate-like Bi-2212 grains, often arranged in 1-5 µm thick colonies that share a common c-axis with [001] twist boundaries. Although the c-axis is often aligned perpendicular to the wire axis, there is no azimuthal texture. Despite this absence of long-range texture, powder-in-tube (PIT) Bi-2212 round
wire can carry remarkably high $J_c$ values ($\sim 1 \times 10^5$ A/cm$^2$ at 45 T and 4.2 K)$^9$. The combination of high $J_c$ and poor texture suggests that GB transport in Bi-2212 round wire is much easier than in Bi-2223 and YBCO.

Partial-melt processing (see the typical multistep process in Fig. 1) is vital to develop high $J_c$.$^{10}$ The conductor whose filament powder starts as essentially single-phase Bi-2212 is heated above the Bi-2212 peritectic temperature to melt the filaments, producing a liquid containing all elements including Ag, alkaline earth cuprate ([(Sr,Ca)$_{14}$Cu$_{24}$O$_x$], and copper-free phase (Bi$_{12}$Sr$_{2}$Ca$_{10}$O$_x$) mixture. Slow cooling, in this case 2.5 °C/hr, solidifies this mixture and below $\sim$872 °C Bi-2212 grains nucleate. Much discussion on improving conductor $J_c$ deals with manipulating the melt phase assemblages.$^{11}$ Here, we concentrate on the final portion of the heat treatment, which occurs after forming the Bi-2212 network, where we enhance the superconducting connectivity by slow cooling in an O$_2$-rich atmosphere.

We quenched 4 cm long sections of a Ag-sheathed wire containing 7 bundles of 85 Bi-2212 filaments fabricated by Oxford Superconducting Technology$^9,12$ at multiple points (Q836C means quenching from 836 °C) in the process using brine as the quench medium to preserve the high temperature microstructures and electromagnetic properties, without introducing damage that might reduce $J_c$.$^{13}$ Thus we could directly correlate the superconducting properties to the high temperature state.

Microstructures were carefully examined and phase chemistry was determined using a field emission scanning electron microscope. The important point is that no observable change in the phase state occurred below the highest temperature examined here, 836 °C. $T_c$ was evaluated from zero-field-cooled magnetic moments measured in a SQUID magnetometer on 5 mm long samples with the wire axis parallel to $\mathbf{H}$. The irreversibility field $H_{irr}$ was approximated by linear extrapolation of the Kramer function $\Delta M^{0.5} H^{0.25}$ to zero, defining $H_k$. $\Delta M$ is the hysteretic magnetization, which is proportional to $J_c$. 5 mm long samples were measured in a 14 T vibrating sample magnetometer with the wire axis perpendicular to $\mathbf{H}$ so that currents propagate along the wire axis across many GBs. The inter- and intra-grain contributions to the hysteretic moment $\Delta M$ were deduced from the remanent
moment $m_R(H_a)$, determined in the SQUID magnetometer by exposing sample to incrementally increasing magnetic field $H_a$ followed by removal of the field and measurement of the remanent moment $m_R$. Magnetic flux first enters at weak regions such as GBs and finally into the grains, $m_R(H_a)$ in each case being given by the product of the screening currents $I_c$ and the length scale of these currents. Differentiation of $m_R(H_a)$ often shows two distinct peaks corresponding at low fields to intergrain currents circulating across GBs, while the higher-field peak corresponds to a combination of intragrain currents of high $J_c$ and/or well connected current paths with long length scales. The transport $J_c$ was determined at an electric field criterion of $10^{-6}$ V/cm with field perpendicular to the wire axis at 4.2 K using the Bi-2212 cross-section before reaction as the normalizing area.

Figure 1 compares the transport $J_c$ at self field and 5 T at 4.2 K for each of the 3 quenched samples (836, 650, and 330 °C), together with a fully processed sample (FP) and the sample that was quenched from 836 °C and then given a final low temperature post-anneal (400 °C, 30 hr) in 1 bar flowing O$_2$ (Q836C+PA). We emphasize that there was no visible difference in the phase state and grain structure of these samples, since the Bi-2212 conversion process was complete at 855 °C, before any quenching. Fig. 1 shows that this slow cool at 170 °C/hr in 1 bar flowing O$_2$ from 836 °C dramatically enhanced $J_c$ (4.2 K, 5 T) from 0.7 to $1.4 \times 10^5$ A/cm$^2$. Self field and 5 T $J_c$ are raised similarly.

Figure 2 shows that as the quench temperature decreases, the transition loses its onset kink and $T_c$ monotonically decreases from ~92 K (836 °C) to ~83 K (< 480 °C), indicating strong oxygen pickup, since $T_c$ of cuprates is a parabolic function of hole concentration that increases with oxygen content $\delta$ in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$. $\delta$ strongly depends on temperature, increasing from 0.2 at 830 °C to 0.25 at 300 °C in 1 bar oxygen. However, all transitions are broad, partly due to small filament dimensions (~20 μm), as well perhaps due to residual compositional inhomogeneities, preferential flux penetration at high-angle grain boundaries, Bi$_2$(Sr,Ca)$_2$CuO$_x$ (Bi-2201) intergrowths, or other secondary phases, and voids. The Q836C+PA sample has the lowest $T_c$ with an onset of 80 K, indicating that it has the highest oxygen concentration.
Figure 3 plots $H_k(T)$ which exhibits the usual behavior of $H_m(T)$, increasing steeply around 20 K.\textsuperscript{17} At 20 K, $H_m(T)$ increased from $\approx 5.6$ T for Q836C to 7.4 T for fully processed wire, while the Q836C+PA sample shows the highest $H_k(20 \text{ K})$ of 8.1 T. This enhancement is explained by a reduced intra-grain electronic anisotropy brought on by the increased carrier density of the overdoped state.\textsuperscript{18, 19}

Figure 4 shows that the remanent current flow paths produce two well separated peaks in $\frac{dm_B}{d \log H_a}$. It is striking that low temperature oxygenation preferentially enhances the first peak in which intergrain paths dominate. The clear implication is that the long-range current flow across GBs is enhanced by oxygenation.

Our central result is that low temperature oxygenation of a macroscopically untextured, round-wire multifilamentary Bi-2212 conductor produces a more than 2 fold enhancement of the in-field $J_c$ (Fig. 1). These treatments enable the high $J_c$ values needed for very-high-field magnets, as demonstrated by the generation of 2.5 T in a 20 T background field\textsuperscript{20} and 1 T in a 31 T background field\textsuperscript{21}, 32 T being a field more than 50\% higher than can be generated with any Nb-based magnet. This oxygen pick up overdopes the Bi-2212 phase, decreasing $T_c$ from 92 to 80 K (Fig. 2), but in all other respects enhancing the superconducting properties (Figs. 1-4). Especially valuable to $J_c$ may be the connectivity enhancement shown in Fig. 4.

The mechanisms of decreased current transport through planar cuprate GBs have been extensively studied. Cuprate GBs develop an increasingly suppressed superconducting order parameter (OP) and $J_c$ as $\theta$ increases.\textsuperscript{3} This OP suppression is amplified by the extra ionic charge, band bending, and strain-driven O$_2$ depletion in the vicinity of the GB, all of which lead to the GB being underdoped with respect to the grains and closer to the parent non-superconducting state. Neither Bi-2223 nor YBCO can be more than lightly overdoped, thus their GBs are underdoped. The benefits of overdoped GBs are seen in the properties of Ca-doped YBCO, because Ca does allow carrier overdoping of the GB\textsuperscript{22-24}, and also in some bulk Bi-2212 bicrystal studies\textsuperscript{25}. The striking present result is that overdoping an untextured Bi-2212 wire makes a hugely positive influence on $J_c$. The poorly oxygenated Q836C and Q650C wires show a characteristic shoulder at 60-82 K in the $m(T)$
curves (Fig. 2), suggesting a decreased $T_c$ at hole-deficient Bi-2212 grain boundaries. Lower-temperature oxygenation removes this shoulder and sharpens the $T_c$ transition, while reducing the $T_c$ onset. We emphasize that the resulting $J_c$ values of $10^5$ A/cm$^2$ or more are practical values that now enable the next generation of very high field magnets,$^{20, 21}$ which makes this overdoping route to a round wire conductor of great practical and scientific interest.

This work was supported by U. S. National Science Foundation Division of Material Research through DMR-0654118 and the State of Florida. The authors are grateful to Van S. Griffin, Natanette C. Craig, and Bill Starch for technical assistance.

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Figure Captions:

Fig. 1 (Color online) Significant increases occur in the self field and 5 T, 4.2 K transport $J_c$ of Bi-2212 round wire in the final stage of the partial-melt process (inset). In flowing 1 bar $O_2$, samples were melted at a maximum temperature of 894 °C and slowly cooled at 2.5 °C/hr to 836 °C, where they were annealed for 48 hr before being cooled at 170 °C/hr to room temperature. Samples were quenched at 836 °C, 650 °C, and 330 °C. A fully-processed (FP) wire and an oxygen-rich sample, which was quenched at 836 °C then post annealed at 400 °C for 30 hr in 1 bar flowing $O_2$, are also shown. These samples are referred to Q836C, Q650C, Q330C, FP, and Q836C+PA. The dashed lines are given to guide the eye.

Figure 2 (Color online) Zero-field-cooled magnetic moments of Ag-sheathed Bi-2212 multifilament round wire Q836C, Q650C, Q330C, FP, and Q836C+PA induced by warming in a field of 1 mT applied parallel to the wire axis, indicates that significant oxygen overdoping occurs during the final cooling to room temperature.

Figure 3 (Color online) Kramer irreversibility field as a function of temperature for Q836C, Q650C, Q330C, FP, and Q836C+PA. Inset shows our method of determining $H_K$.

Figure 4 (Color online) Dependence of the remanent magnetic moment $m_R$ (inset) and its derivative for the Bi-2212 round wires as measured for increasing fields applied parallel to the wire axis at 5 K. Note that the greatest connectivity is shown by sample Q836C+PA.
Figure 1
Figure 3
Figure 4